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16. ABSTRACT The report gives results of a phosphate fertilizer industry study to evaluate multimedia control technology, identify information gaps, and define needed RDandD projects. The following manufacturing processes were covered: wet process phosphoric acid, superphosphoric acid, diammonium phosphate, and normal and triple superphosphate. Air emission control technology, based largely on using wet scrubbers, is adequate for control of fluoride and particulate and is used throughout the industry. The cross-flow packed scrubber appears to be the best and applies to all processes. The gypsum pond appears to be the major environmental concern: main problems are fluoride emissions to the atmosphere and possible leaching of fluoride, phosphate, and radioactive substances. None of the several control alternatives are economically attractive. RDandD projects identified and defined in this study are: (1) an epidemiologic study of the industry; (2) studies of gypsum pond emissions and chemistry; (3) an evaluation and optimization of wet scrubbers; (4) a study of the atmospheric interaction and dispersion modeling of ammonia/sulfuric acid mist; (5) a demonstration of a dry system for fluoride removal; and (6) an evaluation of the Kimre mist eliminator.

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Phosphoric Acids		Phosphate Fertilizers	07B	
Fluorides		Diammonium Phosphate		
Dust		Particulate	11G	
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1.0 EXECUTIVE SUMMARY

The Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency has the responsibility for ensuring that pollution control technology is available for stationary sources to meet air, water and solid waste legislation. The purpose of this study was to evaluate control technology for the phosphate fertilizer industry. The evaluation covered five fertilizer manufacturing processes: wet process phosphoric acid, superphosphoric acid, diammonium phosphate, normal superphosphate and triple superphosphate.

1.1 Phosphate Fertilizer Processes and Emissions

Wet process phosphoric acid is an intermediate product in the manufacture of phosphate fertilizer. Most current processes use the dihydrate process in which phosphate rock is treated with sulfuric acid with gypsum as the major by-product. Fluosilicic acid can also be recovered as by-product resulting in a 50 percent reduction in the average emission of fluorides.

Superphosphoric acid is produced by further concentration of the wet process phosphoric acid using vacuum evaporation or submerged combustion. Seventy-five percent of the total production of superphosphoric acid is prepared using either the falling film (Stauffer) or the forced circulation (Swenson) version of the vacuum evaporation process.

Diammonium phosphate is manufactured through the reaction of anhydrous ammonia with phosphoric acid. TVA's process is the most frequently used while the Dorr-Oliver process has limited application. Normal superphosphate is produced through the reaction between ground phosphate rock and sulfuric acid. Most of its production has been recently replaced by diammonium phosphate and triple superphosphate.

Triple superphosphate is produced through the reaction between ground phosphate rock and phosphoric acid. Run-of-pile triple superphosphate is manufactured by a process similar to normal superphosphate while the TVA or Dorr-Oliver process is used for the production of granular triple superphosphate.

Table 1-1 summarizes air emissions from all five phosphate fertilizer processes. The emissions consist primarily of particulate and gaseous fluorides and some sulfur dioxide. The particulate consists of unreacted rock, final products, and insoluble salts and can include liquid phosphoric acid aerosols and mists. The major gaseous compounds are hydrofluoric acid (HF) and silicon tetrafluoride (SiF_4). The major sources of fluoride emission in the phosphate fertilizer industry are uncontrolled emissions from normal superphosphate curing buildings and fugitive gypsum pond emissions consisting primarily of HF.

TABLE 1-1. EMISSION CHARACTERISTICS FOR PHOSPHATE FERTILIZER PROCESSES AT AVERAGE PLANTS (1)

Process	Emission point	Emission species	Controlled emission factor, g/kg P_2O_5
Phosphoric acid	Rock unloading	Particulate	0.15 ± 250%
	Rock transfer and storage	Particulate	0.045 ± 180%
	Wet scrubber system	Particulate	0.054 ± 164%
		Fluoride	0.010 ± 47%
		Sulfur oxides	0.032 ± 200%
Superphosphoric acid	Wet scrubber	Particulate	0.011 to 0.055
		Fluoride	0.0073 ± 71%(a)
Ammonium phosphate	Product sizing and material transfer	Particulate	1.1(b)
	Total process emissions(c)	Particulate	0.15 ± 120%
		Fluoride	0.038 ± 30%
		Ammonia	0.068 ± 75%
Normal superphosphate	Rock unloading	Particulate	0.28(a)
	Rock feeding	Particulate	0.055 ± 180%
	Mixer and den	Particulate	0.26 ± 86%
		Fluoride	0.10 ± 120%
	Curing building(d)	Particulate	3.6(d)
		Fluoride	1.9 ± 120%(d)
Run-of-the-pile triple superphosphate	Rock unloading	Particulate	0.07(a)
	Rock feeding	Particulate	0.014 ± 170%
	Cone mixer, den, and curing building	Particulate	0.10 ± 50%
		Fluoride	0.10 ± 40%
Granular triple superphosphate	Rock unloading	Particulate	0.09(a)
	Rock feeding	Particulate	0.017 ± 180%
	Reactor, granulator dryer, cooler, and screens	Particulate	0.05 ± 320%
		Fluoride	0.12 ± 30%
		Sulfur oxides	1.86(e)
	Curing building	Particulate	0.10 ± 240%
		Fluoride	0.018 ± 40%
Fertilizer complex	Gypsum pond	Fluoride	0.50 (0.025 to 2.5)(f)

---

[a] Only two data points; uncertainty based on standard deviation.

[b] No data available on fugitive particulate emissions; engineering estimate for uncontrolled emissions based on similar processes.

[c] Average process controlled by integrated control system with a single emission point.

[d] Uncontrolled emission factors because curing building emissions are not normally controlled.

[e] Worst case estimate based on fuel oil sulfur content.

[f] Emissions from gypsum pond are uncontrolled and vary widely depending on pond conditions.

1.2 Control Technologies

1.2.1 Air Emission Control Technology

Air emission control technology in the phosphate fertilizer industry consists almost entirely of wet scrubbers. The most widely used scrubbers are the cyclonic spray, cross-flow packed and Venturi scrubbers. Wet scrubbers have an advantage over dry gas cleaning devices such as filters in that they can simultaneously remove particulate and gaseous emissions. The major gaseous pollutants from phosphate fertilizer manufacturing are fluorides consisting primarily of HF and SiF_4. Most scrubbers use gypsum pond liquid as a scrubbing liquid. Since fluorides are readily soluble in the scrubbing liquid, absorption is gas phase controlled. Four to six transfer units are normally sufficient for over 95% removal efficiency.

The collection of particulate in wet scrubbers is based on the mechanisms of inertial impaction, interception and diffusion. The major parameters that dictate particulate removal efficiency are particle size, pressure drop and liquid to gas ratio.

Table 1-2 shows the combination of wet scrubbers used for removal of fluorides in the five phosphate fertilizer processes. As a rule, primary scrubbers are designed for particulate removal while secondary scrubbers remove most of the fluorides.

Recent findings indicate that fluorides emitted from diammonium phosphate consist partially of submicron particulate. Conventional wet scrubbers have the lowest efficiency on particles whose size is between 0.2 to 1.0 microns so that a scrubber using a removal mechanism other than those mentioned above is needed for effective control. Two such relatively new devices are used in the phosphate fertilizer industry: one is based on nucleation while the other uses electrostatic charging as a mechanism for particulate removal.

Several scrubber vendors supply equipment to the phosphate fertilizer industry and most of the controlled sources are now in compliance with emission regulations. Environmental Elements Corporation and The Ducon Company are representatives of suppliers of large installations while the Ceilcote Company and Heil Process Equipment Company represent suppliers of smaller installations. Davy Powergas is one of the major engineering firms designing phosphate fertilizer plants. They also design their own scrubbers. In the past Davy Powergas has worked closely with Teller Environmental Systems on the design of air emission control equipment, specifically cross-flow scrubbers.

The review of air emission control technology carried out for this project indicates that adequate technology is available for control of gaseous and particulate emissions from phosphate fertilizer plants. The only exceptions are normal and triple superphosphate storage facilities. The use of wet scrubbers at these facilities would result in significant reduction of fluoride emissions. Further reduction of emissions is achievable through recovery of fluosilicic acid, for which the recovery technology is available, but the market for the acid appears to be rather narrow.

TABLE 1-2. SUMMARY OF FLUORIDE EMISSION CONTROL EQUIPMENT FOR FIVE PHOSPHATE FERTILIZER PROCESSES

Process	Fluoride Emission Standard Grams (F-) per Kilogram of P_2O_5	Required Efficiency %	Types of Scrubbers Used	Best Control Technology
Wet process phosphoric acid	0.01	99	Cross-flow packed, Water-actuated Venturi, Centrifugal spray	Cross-flow packed
Super phosphoric acid	0.005	50	Water-actuated Venturi, Conventional Venturi, Impingement	Cross-flow packed
Diammonium phosphate	0.03	85	Primary Conventional Venturi, Cross-flow packed, Two-stage Cyclonic Secondary Cross-flow packed, Two-stage cyclonic, Two-stage Venturi	Primary Coaxial or Cross-flow packed Secondary Nucleation or Cross-Flow packed
Triple superphosphate	0.1	99.6	Primary Cyclonic, Venturi, Spray Secondary Cyclonic, Cross-flow packed	Primary Venturi Secondary Cross-flow packed
Normal and triple superphosphate storage (granular)	0.0025	90	Spray, Cyclonic	Cross-flow packed

1.2.2 Gypsum Pond Emission and Controls

The gypsum pond is an integral part of the phosphate fertilizer manufacture wastewater treatment scheme and it serves two functions. It is a settling and storage area for waste gypsum and fluorides and it provides an area for evaporative cooling of the pond water. It is also used as a scrubbing liquid in wet scrubbers for control of air emissions. Gypsum pond water is a complex mixture of various chemical species. Its pH is about 1.5 and the fluoride concentration ranges between 4,000 and 10,000 ppm. Fluoride concentration in ponds is stabilized due to the fixation of fluorides in insoluble species like chukhrovite or ralstonite. The chemistry of fixation is rather complex and only partially understood, but it appears that the concentration of aluminum and magnesium plays an important role. Two major environmental concerns regarding gypsum ponds are emissions of fluorides to the atmosphere and possible leaching of radioactive substances, fluorides and phosphorus compounds to groundwater supplies and watercourses.

Gypsum pond atmospheric emissions have been calculated and measured and fluoride concentration above these ponds is in the order of tens of ppb. Based on gas-liquid vapor pressure equilibria studies and in-field measurements with EPA's ROSE (Remote Optical Sensing of Emissions) instrumentation, it can be concluded that HF is the major fluoride compound emanating from the gypsum pond. The estimated emission rates from gypsum ponds are in the range of 0.2 to 7.1 lb/acre-day. Consequently, fugitive fluoride emissions from the gypsum pond at many plants appear to surpass the quantities from the controlled stationary sources.

There are virtually no data on leaching of fluorides, phosphates and radium from gypsum ponds and stacks. It appears that contamination of deep aquifers is not occurring because percolation through clayed sediments under ponds is very slow. Only some local contamination of the water table aquifer occurs at some sites. A study currently underway should determine distribution of contaminants around a gypsum pond.

The pond water is reused for wet scrubbing and processing so that discharge is needed only when there is a rainfall in excess of evaporation. In order to meet EPA discharge regulations, two-stage liming combined with settling is needed. The cost of two-stage liming is relatively high so it cannot be used as a means of reducing fluoride emission from gypsum ponds. There are several alternatives for control of these emissions:

1. Two pond system
2. Kidde process
3. Swift process
4. Liming of cooling ponds
5. Dry conveyance of gypsum to stacks
6. Phosphate rock calcining
7. Change to hemi/dihydrate process
8. Use of algae
9. Use of dry systems for air emission control

A first step in controlling fluoride emissions from gypsum ponds would include segregation of gypsum and cooling ponds. The gypsum pond is substantially smaller and pond segregation is a necessary part of applying control options 2 through 5. Table 1-3 gives information on five gypsum pond fluoride control alternatives. The economics of a change to the hemi/dihydrate process used overseas is questionable with low cost and lower quality U.S. rock. Use of algae is at the scientific feasibility evaluation stage. The dry chromatographic technique has been used in secondary aluminum plants and appears to be applicable to phosphate fertilizer plants.

1.2.3 Solid Waste Control

The three sources of solid waste in the phosphate fertilizer industry are by-product gypsum, sludge and wet scrubber liquor. The solid waste can be disposed through use of gypsum ponds and stacks, abandoned mine pits, or through sea disposal. In the U.S. more than 90% of the plants use the gypsum pond-stack technique.

The planning and building of a gypsum pond-stack system requires several steps, including: evaluation of climatic and process constraints, sizing, field evaluation of the subsurface conditions of a tentative site, final site selection, conceptual and detailed design, and actual building. As a rule two ponds are used; one is active while the other one is drained. Although several potential solid waste resource recovery methods are technically feasible, none is economical. The major environmental concern regarding the gypsum pond-stack system is the groundwater contamination discussed earlier. Furthermore, gypsum stacks are sources of low level radioactivity and EPA has classified them as special waste under the Resource Conservation and Recovery Act (RCRA).

1.3 Recommended RD&D Projects

One of the major objectives of this study was to identify gaps in information and to recommend RD&D projects regarding evaluation of control technology in the phosphate fertilizer industry. The following discussion outlines the recommended projects:

1. Epidemiological Study of the Phosphate Fertilizer Industry

   In order to obtain information on the health hazards of the phosphate fertilizer industry, a pilot epidemiological study is recommended. The general strategy should consist of evaluation of routinely collected data on mortality and morbidity. Special emphasis should be on cancer because of the low level radioactivity of gypsum ponds and stacks, and possible leaching of radioactive substances. If the pilot study shows higher mortality or morbidity rates in the "exposed" population, a follow-up study including evaluation of specifically collected data should be carried out.

TABLE 1-3. INFORMATION ON FIVE GYPSUM POND FLUORIDE CONTROL ALTERNATIVES (BASED ON 1,000 TPD P_2O_5 PLANT)

Process	Where Applied	Fluoride Removal Efficiency %	By-Product	Total Capital Investment $ MM	Technical Pros and Cons	
Kidde	Barometric condensers	95-98	$(NH_4)_2S_iF_6$	2.6	Improved quality of phosphoric acid. Increased recovery of fluoride.	No full scale installation.
Swift Absorption	Barometric condensers	90	$H_2S_iF_6$	1.3	$H_2S_iF_6$ recovery may make process profitable.	Process is rather complex.
Liming	All cooling pond water	90	None	2.1	Simplest process.	Secondary environmental problems.
Conveyor	Gypsum filter after acidulation	N/A	None	1.1	Benefits/disadvantages difficult to determine	
Pre-Calcination of Rock	Crushed phosphate rock	N/A	None	23.8	Removes fluorides before processing.	High cost.

2. Studies of Gypsum Pond Emissions and Chemistry

The gypsum pond appears to be a major environmental concern of the phosphate fertilizer industry, yet the existing information on its emissions and chemistry is scarce.

A study of gypsum pond chemistry is recommended since it could lead to reduced fluoride emissions. The major objective of such a study would be an understanding of the factors governing the fixation of fluorine in the pond and cake.

A study of gypsum pond fluoride liquid-vapor equilibria is also recommended since no reliable data exist. Although some in-field measurement of fluoride emission from gypsum ponds has been carried out, more data are needed for a reliable estimate of emission rates. A major purpose of such measurements would be the correlation of emission rates with atmospheric and plant conditions.

3. Evaluation and Optimization of Wet Scrubbers

There is little reliable information on the performance of wet scrubbers and two performance evaluations are recommended. The first is scrubber optimization through fractional factorial design experiments. The main objective should be to optimize removal of fluoride and particulate while minimizing energy consumption in wet scrubbing (preferably for the cross-flow packed type scrubber).

The second study is the performance evaluation of ionized wet scrubbers. The main purpose of this evaluation would be to measure the particulate removal efficiency as a function of the particle size distribution. The verification of the claimed high efficiency of this scrubber in the health-related submicron particle range is very important since its application goes beyond the phosphate fertilizer industry.

4. Ammonia-Sulfuric Acid Mist Interaction Atmospheric Chemistry and Dispersion Modeling Study

In the past some diammonium phosphate plants have experienced a downwind opacity problem due to formation of ammonium sulfate particles. An experimental study of the interaction between gaseous ammonia and sulfuric acid mist in a smog chamber is recommended. A model describing the interaction of ammonia and the acid mist plume incorporating an aerosol dynamics model should be developed in this study.

5. Demonstration of Dry Fluoride Removal System

The demonstration of a dry fluoride removal system is recommended since its use could reduce the need for gypsum ponds. Several secondary aluminum plants now use this system in which fluoride and fine particulates lates are removed simultaneously. A major objective of this project would be to demonstrate the applicability of the dry system in a phosphate fertilizer plant and to obtain design parameters for the design of a full scale system. A pilot model capable of handling 3000 NCMH (about 1750 SCFM) applied on diammonium phosphate emissions is recommended.

6. Optimization of Kimre Mist Eliminator

An efficiency evaluation of the Kimre mist eliminator is recommended since several scrubber installations in the phosphate fertilizer industry have been recently retrofitted with this device. The main purpose of the evaluation program would be to verify the claimed high efficiency in aerosol removal and to establish optimum operating conditions.

1.4 References

1. Nyers, J.M., et al, Source Assessment: Phosphate Fertilizer Industry, EPA 600/2-78-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1978, 185 pp.

2.0 CONCLUSIONS

There are two main conclusions from this evaluation of control technology for the phosphate fertilizer industry. First, there is adequate control technology for application to gaseous emissions from all five studied processes, and secondly, gypsum pond emissions appear to be the major environmental problem facing the industry since there are no simple nor economical means to control such emissions. The following are more detailed conclusions:

1. Wet scrubbers, represented primarily by cross-flow packed scrubbers, Venturi scrubbers and cyclonic spray scrubbers, are widely and successfully used for control of air emissions consisting primarily of fluorides and particulate. A review of four representative vendors indicates that there are several types of scrubbers with adequate efficiency to comply with existing emission regulations.

2. Cross-flow packed scrubbers appear to be the best control alternative applicable to all five processes since they demonstrate high efficiency and relatively low capital, operating and maintenance costs. One of the new applications in the industry is the use of ionized wet and nucleation scrubbers which are effective in removal of submicron particulate matter. The dry chromatographic system used in some other industries also seems to be applicable to the phosphate fertilizer industry.

3. The only major reduction of fluoride emissions from stationary sources is achievable through control of emissions from Run of Pile - Triple Superphosphate (ROP-TSP) storage facilities which are, as a rule, uncontrolled, and through recovery of fluosilicic acid which would reduce fluoride input to gypsum ponds.

4. In spite of the large numbers and size of wet scrubbing installations in the phosphate fertilizer industry, reliable data on scrubber performance are scarce. Tests based on factorial experiment design are needed to develop reliable data and assist in optimization of scrubber performance.

5. The emissions from gypsum ponds appear to be the major environmental problem facing this industry. The air emission load consisting primarily of HF seems to be higher per ton of P_2O_5 produced than that from the combined process sources controlled by wet scrubbers.

6. The leaching of radioactive substances, fluorides and phosphorus compounds from gypsum ponds and stacks could result in aquifer contamination. A study presently underway sponsored by the State of Florida and the EPA should determine the distribution of contaminants around a gypsum pond.

7. There are several potential control techniques for application to gypsum pond emissions but none appears to be economically attractive. A first step should include segregation of gypsum and cooling ponds, followed by

some gypsum pond treatment technique. Single liming is probably the simplest treatment method while the Swift process may be economical if all by-product fluosilicic acid can be sold.

8. More research is needed before the environmental impact of gypsum ponds can be fully assessed. The studies should include gypsum pond chemistry, vapor pressure equilibria and correlation of fluoride emissions with plant, pond and atmospheric conditions.

9. Solid waste, consisting primarily of by-product gypsum, appears to be adequately disposed through stacking although there is some concern due to its low level radioactivity.

3.0 RECOMMENDATIONS

In order to further the knowledge of the environmental impact of the phosphate fertilizer industry and specifically to improve the control technology, the following studies are recommended to EPA:

1. An epidemiological study should be carried out to assess the impact of the phosphate fertilizer industry on the population. Special emphasis should be on the mortality and morbidity rates related to low level radioactivity, specifically those related to bone cancer. Only a pilot study is recommended as a first step.

2. Since the gypsum pond appears to be the major environmental concern related to this industry, pond emisssions and chemistry should be studied. Special emphasis should be placed on the chemistry of fluoride fixation in the gypsum pond. An investigation of gypsum pond fluoride liquid-vapor equilibria should be included. Field measurements of gypsum pond fluoride emissions should be carried out in order to correlate these with the plant operating conditions, atmospheric conditions, and gypsum pond characteristics.

3. In order to improve the efficiency and economics of wet scrubbers, two evaluation and optimization studies are recommended. A fractional factorial design experiment is recommended for an evaluation and optimization of a full scale scrubber in a representative plant. A performance evaluation of the ionizing wet scrubber is also recommended with special emphasis on submicron aerosol removal efficiency in a representative DAP plant.

4. A study of the atmospheric chemistry of ammonia-sulfuric acid mist interaction and a dispersion modeling study are recommended in order to better understand and prevent opacity problems occurring downwind from DAP plants.

5. A dry fluoride removal system with a capacity for treatment of 3000 NCMH (1750 SCFM) should be built in order to evaluate its performance in the removal of fluorides and particulate matter.

6. Many scrubbing systems in the phosphate fertilizer plants have been recently retrofitted with Kimre mist eliminators. An evaluation of this equipment is recommended. Special emphasis should be placed on obtaining data on performance and optimization.

4.0 PROCESS AND EMISSION DESCRIPTION FOR FIVE PHOSPHATE FERTILIZER MANUFACTURING PROCESSES

The phosphate fertilizer industry uses phosphate rock as its major raw material. The primary objective of this industry is to convert the fluorapatite ($Ca_{10}(PO_4)_6F_2$) in phosphate rock to soluble P_2O_5, a form readily available for plant use. The usual method of making the P_2O_5 content of phosphate rock available to plants is by treatment with a mineral acid-sulfuric, phosphoric or nitric (1). Figure 4-1 shows the major phosphate rock processing steps (2).

Phosphate fertilizer manufacturing processes are described in detail in several major references (1), (3), (4), and (5). For a better understanding of emission control technology, this section will briefly cover five processes with emphasis on emissions. Detailed discussions of control technology are presented in Sections 5, 6, and 7.

4.1 Wet Process Phosphoric Acid (WPPA)

4.1.1 WPPA Process Description

Phosphoric acid is an intermediate product in the manufacture of phosphate fertilizer. It is subsequently consumed in the production of triple superphosphate, ammonium phosphate, superphosphoric acid, dicalcium phosphate and complex fertilizer.

Most current processes use the dihydrate process in which phosphate rock is treated with sulfuric acid under conditions where gypsum ($CaSO_4 \bullet H_2O$) is precipitated (1).

The overall reaction in the dihydrate process is described by the following equation:

$$3\,Ca_{10}(PO_4)_6F_2 + 30\,H_2SO_4 + SiO_2 + 58\,H_2O \rightarrow 30\,CaSO_4 \bullet 2\,H_2O + 18\,H_3PO_4 + H_2SiF_6$$

Major variations of the dihydrate process are the Prayon, Swenson, Dorr-Oliver and Singmaster processes, with Prayon (designed by Davy Powergas) being used most frequently.

Figure 4-2 presents a flow diagram for a typical wet process phosphoric acid plant.*

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*Unreferenced figures were prepared by TRC based on the open literature diagrams and some proprietary information.

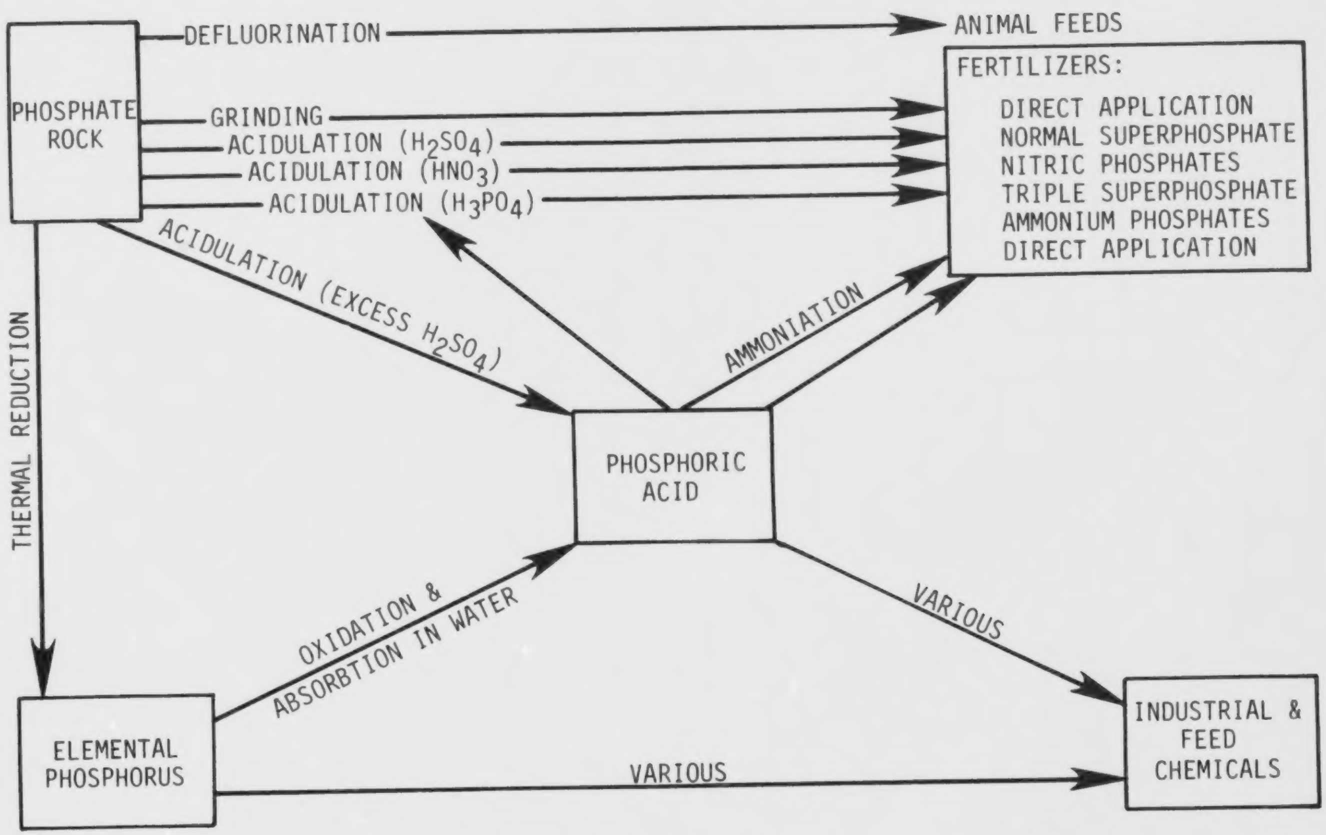
PHOSPHATE ROCK
DEFLUORINATION
ANIMAL FEEDS
GRINDING
ACIDULATION (H_2SO_4)
ACIDULATION (HNO_3)
ACIDULATION (H_3PO_4)
FERTILIZERS:
DIRECT APPLICATION
NORMAL SUPERPHOSPHATE
NITRIC PHOSPHATES
TRIPLE SUPERPHOSPHATE
AMMONIUM PHOSPHATES
DIRECT APPLICATION
ACIDULATION (EXCESS H_2SO_4)
AMMONIATION
THERMAL REDUCTION
PHOSPHORIC ACID
OXIDATION & ABSORBTION IN WATER
VARIOUS
ELEMENTAL PHOSPHORUS
VARIOUS
INDUSTRIAL & FEED CHEMICALS

Figure 4-1: Major Phosphate Rock Processing Steps (2)

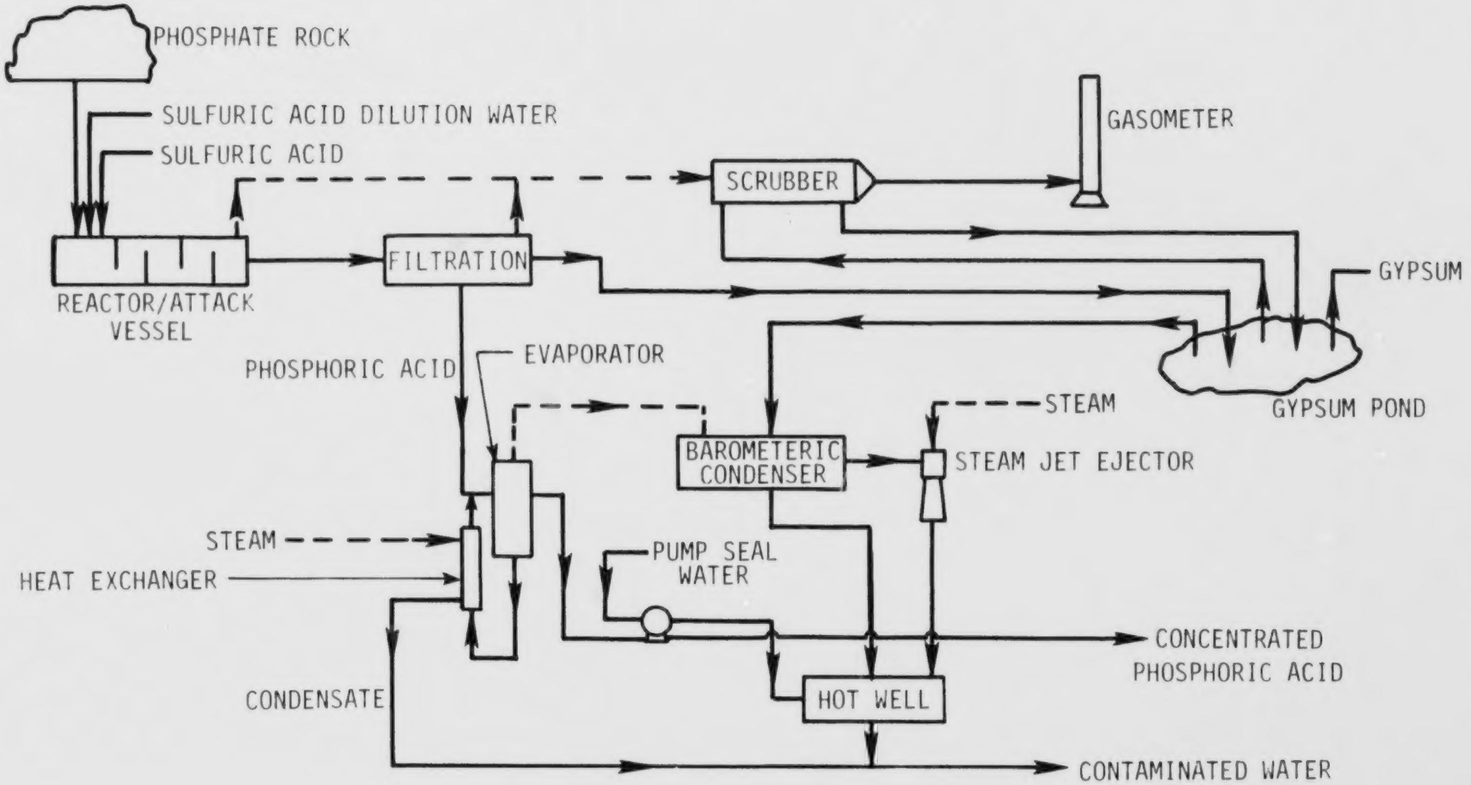
PHOSPHATE ROCK
SULFURIC ACID DILUTION WATER
SULFURIC ACID
GASOMETER
SCRUBBER
REACTOR/ATTACK VESSEL
FILTRATION
GYPSUM
PHOSPHORIC ACID
EVAPORATOR
GYPSUM POND
STEAM
BAROMETERIC CONDENSER
STEAM JET EJECTOR
STEAM
HEAT EXCHANGER
PUMP SEAL WATER
CONCENTRATED PHOSPHORIC ACID
CONDENSATE
HOT WELL
CONTAMINATED WATER

Figure 4-2: Flow Diagram for a Wet-Process Phosphoric Acid Plant

In the WPPA process finely-ground phosphate rock is continuously metered into the reaction vessel and sulfuric acid is added. The reaction vessel has several compartments needed for completion of the reaction, during which the sulfate ion must be closely controlled for a proper crystal growth required for easy filtration. The heat of reaction is removed from the reactor by vacuum flash cooling.

The reaction slurry is filtered in the rotary horizontal tilting-pan vacuum filter. The 32% acid obtained from the filter is concentrated in a two or three stage vacuum evaporator system to about 54%. The evaporators can be equipped with scrubbers for the collection of H_2SiF_6 which can be produced at 20% by weight concentration. This recovery feature is not necessary to the evaporation and is a matter of economics; it would, however, substantially reduce fluoride transfer to a gypsum pond.

Vapors from the vacuum flash cooler are condensed in a barometric condenser and sent to a hot well while the non-condensibles are removed by a steam ejector and are also vented to the hot well.

4.1.2 Emissions from WPPA

Fluoride emissions from wet-process phosphoric acid (WPPA) will vary depending upon the type of rock treated and process used. Gaseous fluorine emissions consist of silicon tetrafluoride generated in the reaction and evaporation phases. Hydrogen fluoride formed in the reactor is converted to SiF_4 according to the reaction (5):

$$4\ HF + SiO_2 \quad SiF_4 + 2\ H_2O$$

Table 4-1* shows a material balance depicting final distribution of the fluorine from the rock. Wet scrubbers are used for control of air emissions at phosphoric acid plants. They will be evaluated in Section 5.

Table 4-2 shows stack height and controlled emission factors for WPPA based on actual data from 10 plants (3). The average emission factors were calculated for plants with and without recovery of by-product fluorine. Results show that the average emission factor for the wet scrubber at plants recovering fluorine is half the amount in plants without recovery.

The emissions of fluorides from gypsum ponds will be evaluated more in Section 6. A close look at Table 4-2 reveals that the gypsum pond is by far the largest source of fluoride emission at the WPPA plant.

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*Metric units of measurement will be used throughout this report except where English units were used in the original citation.

TABLE 4-1. FLUORINE MATERIAL BALANCES FOR WPPA MANUFACTURE (3)

Material Balance	Fluorine, 10^6 g/day				Plant Daily Production, Metric tons P_2O_5	Fluorine Emission Factor g/kg P_2O_5
	Phosphate Rock	Product Acid	Gypsum Slurry And Process H_2O	Air Emission		
A[a]	48.3	36.5	11.8	0.004	368	0.011
B[b]	127.0	16.3	110.7	0.009	907	0.024

[a] Data obtained from the public files at the Florida Department of Environmental Regulations in Winter Haven, October 1976.

[b] Data from Reference (6).

TABLE 4-2. AVERAGE STACK HEIGHTS AND CONTROLLED EMISSION FACTORS FOR WET PROCESS PHOSPHORIC ACID (3)

Emission Point	Stack Height, m	Emission Factor, g/k P_2O_5		
		Total Fluoride	Particulate	SO_x
Wet process phosphoric acid:				
Rock unloading	12	0	0.15 ± 250%	0
Rock transfer and conveying	21	0	0.045 ± 180%	0
Wet scrubber system:-				
Overall		0.010 ± 47%	0.054 ± 164%	0.032 ± 200%
With recovery of fluorine		0.0059 ± 61%	—[a]	—[a]
Without recovery of fluorine		0.012 ± 60%	—[a]	—[a]
Gypsum pond		0.025 to 2.5 (avg 0.50)	0	0

[a] Insufficient data to determine the effect of fluorine recovery on other emission species.

Particulate emissions generated in the reactor consist of unreacted rock and insoluble salts. The particulate emission factor shown in Table 4-2 is based on measurements at five plants.

The origin of SO_x emissions in WPPA manufacture is not clear. The SO_x emission factor in Table 4-2 is based on data from one plant and a Public Health Service document (7).

4.2 Superphosphoric Acid (SPA)

4.2.1 SPA Process Description

Phosphoric acid produced by the wet process is in ortho form and it can be converted to polyphosphoric acid through heating. The chemical reaction occurring during heating is described by:

$$X\ H_3PO_4 \xrightarrow{\Delta} H_{x+2}\,P_x\,O_{3x+1} + (x-1)\ H_2O$$

The product of this reaction is a mixture of orthophosphoric acid and dehydrated acid called superphosphoric acid. WPPA is concentrated to SPA primarily to reduce the cost of transportation, but additional benefits are that SPA is less corrosive and contains fewer impurities than WPPA.

Two commercial processes are used for production of SPA from WPPA: Submerged Combustion (about 25% of the total production capacity) and Vacuum Evaporation (about 75% of the total production capacity).

The Submerged Combustion process accomplishes dehydration by bubbling hot combustion gas through a pool of the acid. It will not be discussed in this report since vacuum evaporation is more commonly used.

Two vacuum evaporation processes are in commercial use:

1. The falling film (Stauffer) process; Figure 4-3
2. The forced circulation (Swenson) process; Figure 4-4

Both processes are similar and use high vacuum concentrators with high-pressure steam to concentrate acid to 70% P_2O_5. Feed acid is introduced into a large volume of recycling product acid to reduce corrosion. In both systems, product acid is pumped to a cooler before being sent to storage or shipped. An appropriate recycle feed ratio is 150:1 in the Swenson process (compared with 80:1 for the Stauffer process). Both the hot well and cooling tank are vented to a wet scrubbing system.

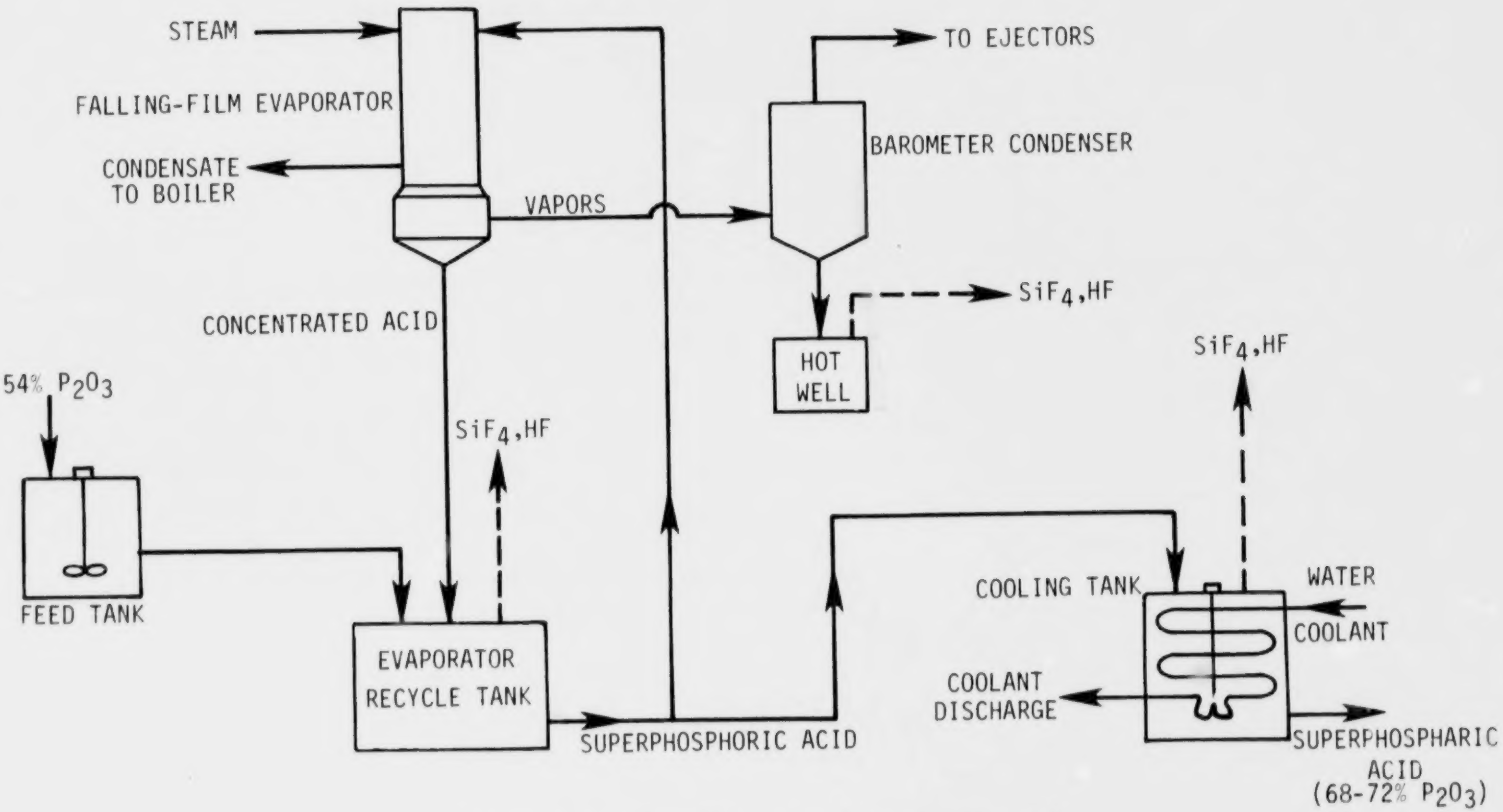
STEAM
FALLING-FILM EVAPORATOR
CONDENSATE TO BOILER
VAPORS
TO EJECTORS
BAROMETER CONDENSER
HOT WELL
SiF_4,HF
CONCENTRATED ACID
54% P_2O_3
FEED TANK
SiF_4,HF
EVAPORATOR RECYCLE TANK
SUPERPHOSPHORIC ACID
SiF_4,HF
COOLING TANK
WATER
COOLANT
COOLANT DISCHARGE
SUPERPHOSPHARIC ACID (68-72% P_2O_3)

Figure 4-3: Stauffer Evaporator Process (8)

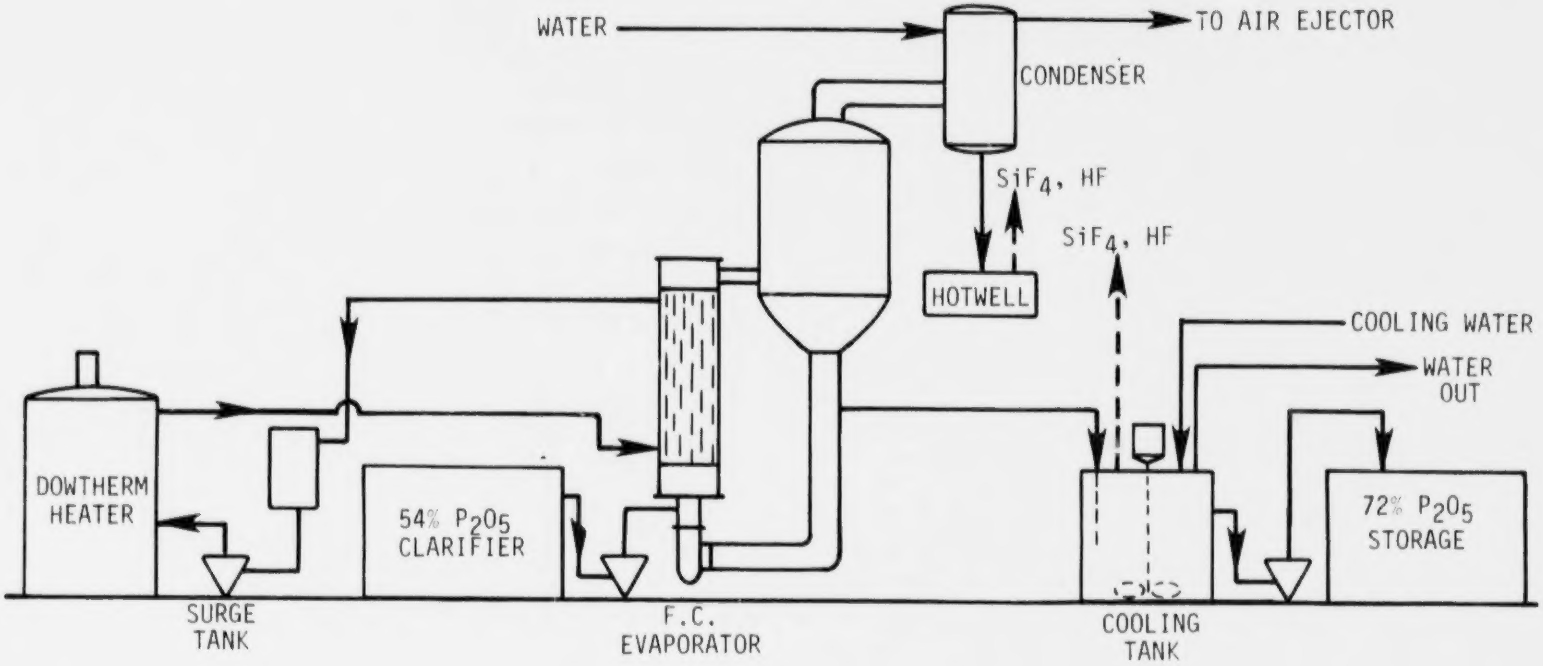
WATER
TO AIR EJECTOR
CONDENSER
SiF$_4$, HF
SiF$_4$, HF
HOTWELL
COOLING WATER
WATER OUT
DOWTHERM HEATER
54% P$_2$O$_5$ CLARIFIER
72% P$_2$O$_5$ STORAGE
SURGE TANK
F.C. EVAPORATOR
COOLING TANK

Figure 4-4: Swenson Evaporator Process (8)

4.2.2 Emissions from SPA

Emissions from the SPA plant consist primarily of gaseous fluorides and particulates. Hydrogen fluoride is the major gaseous pollutant, while particulates are limited to liquid phosphoric acid aerosols and mists produced by the condensation process. The falling film evaporator can generate submicron aerosols which are difficult to remove from the gas stream.

Fluorine emission data for two plants using vacuum evaporation were evaluated by Monsanto (3). The barometric condenser, hot well and product cooling tank are vented to a two-stage wet scrubber. Fluorine emission factors from these plants are 0.0036 and 0.011 g/kg P_2O_5, with an average value of 0.0073 g/kg P_2O_5. One plant reported particulate emissions ranging from 0.011 to 0.055 g/kg P_2O_5.

4.3 Diammonium Phosphate (DAP)

4.3.1 DAP Process Description

The typical ammonium phosphates used as fertilizer contain from 11% to 21% nitrogen and 20% to 55% P_2O_5 (9). In 1975, 84% of total production (on a P_2O_5 basis) consisted of DAP grade.

Diammonium phosphate is manufactured from phosphoric acid and ammonia. The process consists of three basic steps, including reaction, granulation, and finishing operations such as drying, cooling, and screening.

In the first step, anhydrous ammonia is reacted with phosphoric acid to form hot liquid DAP as described by the equation (10):

$$2NH_3 + H_3PO_4 \rightarrow (NH_4)_2\ H\ PO_4 - 81{,}500\ \text{BTU}\ (20{,}529{,}850\ \text{calories})$$

(gas) (liquid) (liquid) (ΔH_R @ 60 F)

The most frequently used process for diammonium phosphate manufacture is TVA's, shown in Figure 4-5. Phosphoric acid is mixed in an acid surge tank with 93% sulfuric acid (used for product analysis control) along with recycle and acid from wet scrubbers. Mixed acids have a P_2O_5 content of 40% to 45% (11). This analysis is attained by mixing unconcentrated filtered WPPA, 28.7% P_2O_5, and concentrated WPPA, 53.3% P_2O_5.

Mixed acids are then partially neutralized with liquid or gaseous anhydrous ammonia in a brick-lined acid reactor. In this agitated atmospheric pressure tank, the mole ratio of NH_3: H_3PO_4 is maintained at 1.3:1.0 to 1.5:1.0. All phosphoric acid and approximately 70% of the ammonia are introduced in this vessel. In this molar range, ammonium phosphates are most soluble, allowing further concentration of solution while maintaining adequate flow characteristics. The heat of reaction is used in this vessel to maintain a temperature of 100°C to 120°C and to evaporate

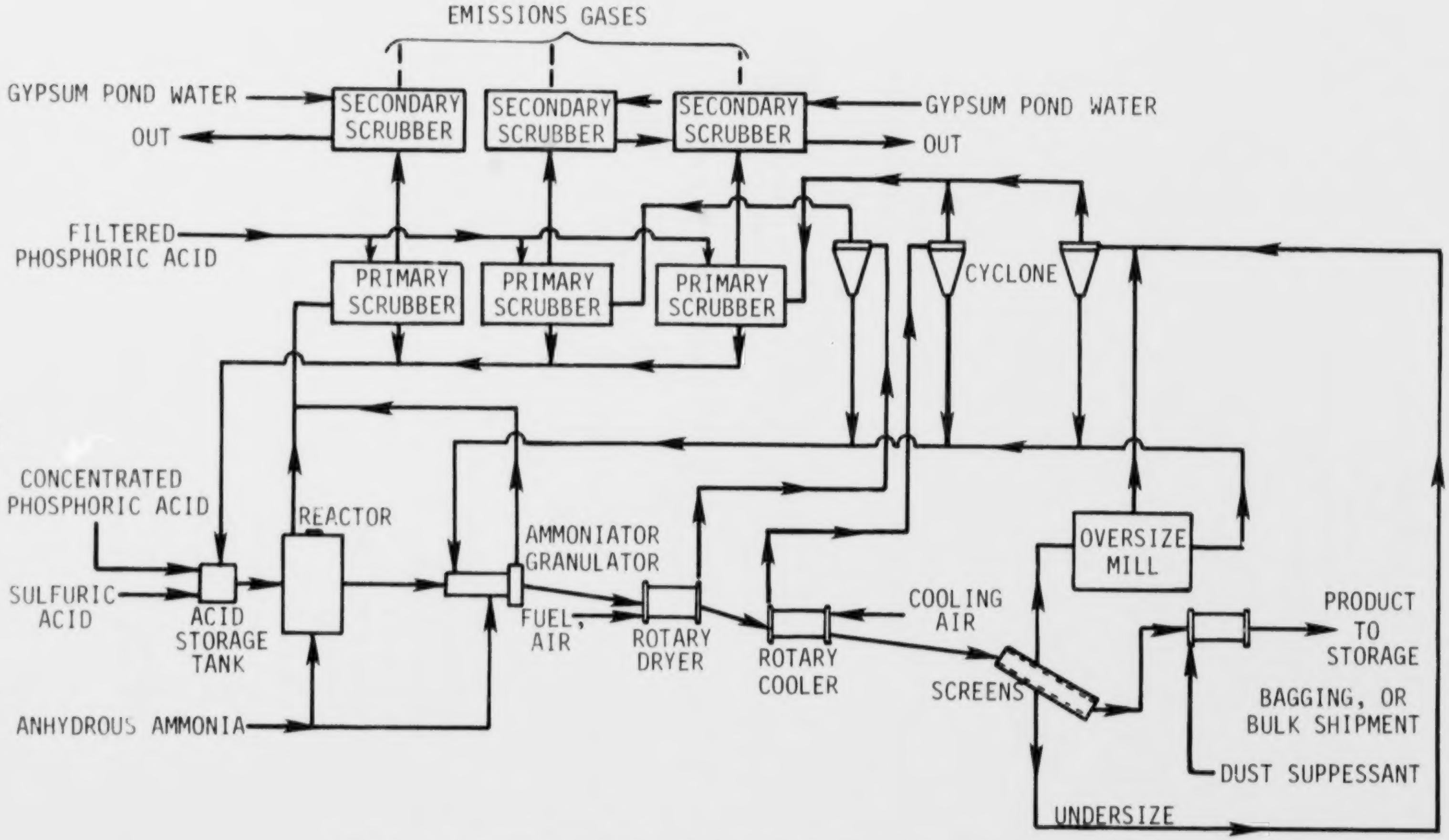
EMISSIONS GASES
GYPSUM POND WATER
OUT
SECONDARY SCRUBBER
SECONDARY SCRUBBER
SECONDARY SCRUBBER
GYPSUM POND WATER
OUT
FILTERED PHOSPHORIC ACID
PRIMARY SCRUBBER
PRIMARY SCRUBBER
PRIMARY SCRUBBER
CYCLONE
CONCENTRATED PHOSPHORIC ACID
SULFURIC ACID
ACID STORAGE TANK
REACTOR
AMMONIATOR GRANULATOR
FUEL, AIR
ROTARY DRYER
ROTARY COOLER
COOLING AIR
SCREENS
OVERSIZE MILL
PRODUCT TO STORAGE
BAGGING, OR BULK SHIPMENT
DUST SUPPESSANT
ANHYDROUS AMMONIA
UNDERSIZE

Figure 4-5: TVA Ammonium Phosphate Process Flow Diagram

excess water. A slurry which is primarily MAP and contains 18% to 22% water is produced and flows through steam-traced lines to the ammoniator-granulator. To assure no leakage from the reactor, the vessel is ventilated with outside air. In theory, the reactor could be designed without ventilation or atmospheric discharge, but in practice, ventilation rates of 57 to 71 m^3/min (standard conditions) are common. Ventilation rate is determined by reactor mechanical design, not process requirements. Ammonia-rich offgases from the reactor at 77°C to 82°C are wet-scrubbed before exhausting to the atmosphere. Primary scrubbers use raw material-mixed acids as scrubbing liquor, and secondary scrubbers use gypsum pond water as scrubbing liquor.

The basic rotary-drum ammoniator-granulator consists of an open-end, slightly inclined rotary cylinder with retaining rings at each end and a scraper or cutter mounted inside the drum shell. Drums vary in diameter from 2 m to 3 m and in length from 3 m to 6 m. A rolling bed of recycled solids is maintained in the unit. Slurry from the reactor is distributed above the bed while the remaining ammonia (approximately 30%) is sparged underneath to bring the final NH_3: H_3PO_4 mole ratio from 1.8:1.0 to 2.0:1.0. Granulation by agglomeration and by coating particles with slurry takes place in the rotating drum and is completed in the dryer. Recycle rates of 2.5 to 4.0 kg recycle/kg product are typical for this type of unit. As with the reactor, the granulator theoretically could be designed without ventilation, but to prevent NH_3 leakage, approximately 8.5×10^{-4} m^3 (standard conditions) per metric ton P_2O_5 air leakage is allowed into the granulator around inlet and outlet connections.

The temperature of granular DAP in the rotary drum reaches 85°C to 105°C, while the temperature of offgases reaches 38°C to 77°C. Ammonia-rich offgases pass through a wet scrubber before exhausting to the atmosphere.

Moist DAP granules are transferred to a rotary oil- or gas-fired cocurrent dryer which reduces product moisture content to below 2%. The product is then cooled to below 35°C. Cooling minimizes caking and product dissociation during storage. The temperature of offgases from the dryer ranges from 82°C to 104°C, and the temperature of offgases from the cooler ranges from 4°C to 27°C. Before exhausting to the atmosphere, these offgases pass through cyclones and wet scrubbers.

Cooled granules pass to a double-deck screen in which oversized and undersized particles are separated from product-sized particles. Some plants screen the product before cooling. DAP product ranges in granule size from 1 mm to 4 mm, with a typical log-normal product size distribution. The oversized granules are crushed, mixed with the undersized, and recycled to the ammoniator-granulator. To reduce DAP dustiness, some manufacturers coat product granules with 0.5% by weight of 10-wt lubricating oil using a rotating dust suppressant system. DAP is either stored, bagged, or bulk-loaded for shipment.

4.3.2 Emissions from DAP

Air emissions sources and their related emission species from DAP are(3):

- Reactor: ammonia, fluorides.
- Ammoniator-granulator: ammonia, fluorides, particulates.
- Dryer: ammonia, fluorides, particulates, combustion gases.
- Cooler: ammonia, fluorides, particulates.
- Product sizing and material transfer: particulates.
- Gypsum pond: fluorides.

Ammonia emissions are due to incomplete chemical reaction and excess free ammonia. While the ammonia emissions alone do not present an environmental hazard, there is a potential additional effect. Almost all DAP plants also manufacture sulfuric acid at the same facility. Under adverse atmospheric conditions, ammonia and sulfuric acid mist can react in the atmosphere. The resulting ammonium sulfate could affect visibility downwind from the plant. The analysis of this potential environmental hazard will be addressed as a proposed R&D project in a separate section (Section 9).

Fluoride emissions originate from the fluoride content of phosphoric acid and consist primarily of silicon tetrafluoride (5). Dryer offgases contain combustion products in negligible quantities. Table 4-3 shows emission factors for ammonium phosphate manufacture. All emissions listed reach the atmosphere through a stack. Product sizing and material transfer process steps produce both stack and fugitive emissions. An uncontrolled emission factor of 2.2 g/kg P_2O_5 for this source has been reported (12). The emission factors in Table 4-3 are based on literature and data on file at the Florida Department of Environmental Regulations, presently located in Tampa, Florida. Total plant stack emission factors were also calculated as (3):

Particulate: 1.5 g/kg P_2O_5
Fluoride (as F): 0.038 g/kg P_2O_5
Ammonia: 0.068 g/kg P_2O_5

Information on fluoride emissions from gypsum ponds, reported as 0.025 to 2.5 g/kg P_2O_5 in Table 4-2 for WPPA, also applies here. One half of forty-eight ammonium phosphate plants produce WPPA. Plants producing only DAP have smaller ponds with lower fluoride emissions (3).

4.4 Normal Superphosphate (NSP)

4.4.1 NSP Process Description

Because of low P_2O_5 content the popularity of NSP has decreased from 68% (total phosphate fertilizer market share) in 1957 to about 18% where it is now stabilized. The two raw materials used in the production of NSP are 65% to 75% sulfuric acid and ground phosphate rock. The basic chemical reaction is shown by the following equation:

TABLE 4-3. EMISSION FACTORS FOR DIAMMONIUM PHOSPHATE PLANTS (3)

Emission Point[a]	Controlled Emission Factors Mean g/kg P_2O_5	Controlled Emission Factors 95% Confidence Interval, % of Mean
Reactor/ammoniator-granulator:		
Fluoride (as F)	0.023	±80
Particulate	0.76	±90
Ammonia	–[b]	–[b]
Dryer/cooler:		
Fluoride (as F)	0.015	±160
Particulate	0.75	±60
Ammonia	–[b]	–[b]
Product sizing and material transfer:		
Fluoride (as F)	0.001	–[c]
Particulate	0.03	–[c]
Ammonia	–[b]	–[b]
Reported as total plant emissions:		
Fluoride (as F)	0.038[d]	±30
Particulate	0.15[e]	±120
Ammonia	0.068	±75

[a] Fugitive emissions are included in the text.

[b] No information available; although ammonia is emitted from these unit operations, it is reported as a total plant emission.

[c] Emission factor represents only 1 sample.

[d] A fluoride emission guideline of 0.03 g/kg P_2O_5 input has been promulgated by EPA.

[e] Based on limited data from only 2 plants.

$$[Ca_3(PO_4)_2]_3 \bullet CaF_2 + 7\ H_2SO_4 + 3\ H_2O \rightarrow 3[CaH_4(PO_4)_2 \bullet H_2O] + 7\ CaSO_4 + 2\ HF$$

Figure 4-6 shows an NSP process flow diagram showing a TVA double conical mixer used by 80% of NSP plants. Ground phosphate rock is fed into the double conical mixer where it is mixed with diluted sulfuric acid. The heat of sulfuric acid dilution serves to heat the sulfuric acid to a proper reaction temperature. The fresh superphosphate discharges from the conical mixer to a pug mill for additional mixing of acid and rock before discharge to a den. NSP product is kept in the den for one hour for solidifying. The cutter slices the solid mass of crude product so that it may be conveyed to the pile storage for "curing." The product takes about 10-20 days to reach an acceptable P_2O_5 content. The hardened run-of-pile (ROP) product obtained in the above process may be granulated. In order to granulate ROP product, it is pulverized and sent to a rotary drum granulator where steam and water are added. The mixture is passed through a rotary dryer and cooler to final storage. Most of the NSP is used in fertilizer mixing plants where it serves as one of the ingredients in preparation of nitrogen-phosphorus-potassium (NPK) mixtures.

4.4.2 Emissions from NSP

The major sources of emissions at an NSP plant are the mixer, the den, and the curing building. Fluoride emissions consisting of hydrogen fluoride and silicon tetrafluoride are controlled by scrubbing with water. Most NSP plants presently practice fluorine recovery, eliminating the need for a gypsum pond (3).

Table 4-4 shows emission factors for an NSP plant based on source test data (3). Data were available for 4 tests for controlled emissions from the curing building, but most emissions from curing buildings are uncontrolled. The emission factor was therefore derived using a control efficiency of 97%.

4.5 Triple Superphosphate (TSP)

4.5.1 TSP Process Description

Triple superphosphate with 45 to 49% P_2O_5 content has replaced most NSP because of transportation economy. Run-of-Pile (ROP) and Granular Triple Superphosphate (GTSP) are two principal types of TSP. Both processes achieve high P_2O_5 content by replacing sulfuric acid with phosphoric acid. The basic chemical reaction is shown by the following:

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 + 3\ H_2O \rightarrow 3\ Ca(H_2PO_4)_2 \bullet H_2O$$

The ROP process is essentially identical to the NSP process shown in Figure 4-6 and will not be discussed here.

TABLE 4-4. EMISSION FACTORS FOR AN AVERAGE NORMAL SUPERPHOSPHATE PLANT BASED ON CONTROLLED EMISSION SOURCES (3)

Emission Source	Emission Factor, g/kg P_2O_5	
	Particulates	Fluorides[a]
Rock unloading	0.28[b]	-[c]
Rock feeding	0.055 ± 180%	-[c]
Mixer and den	0.26 ± 86%	0.10 ± 120%
Curing building[d]	3.6	1.9 ± 120%

---

[a] Fluoride released as a vapor.

[b] Based on two sets of data; therefore 95% confidence limits could not be determined.

[c] Not emitted from this source.

[d] Uncontrolled emission factors since curing building emissions are not controlled at an average plant.

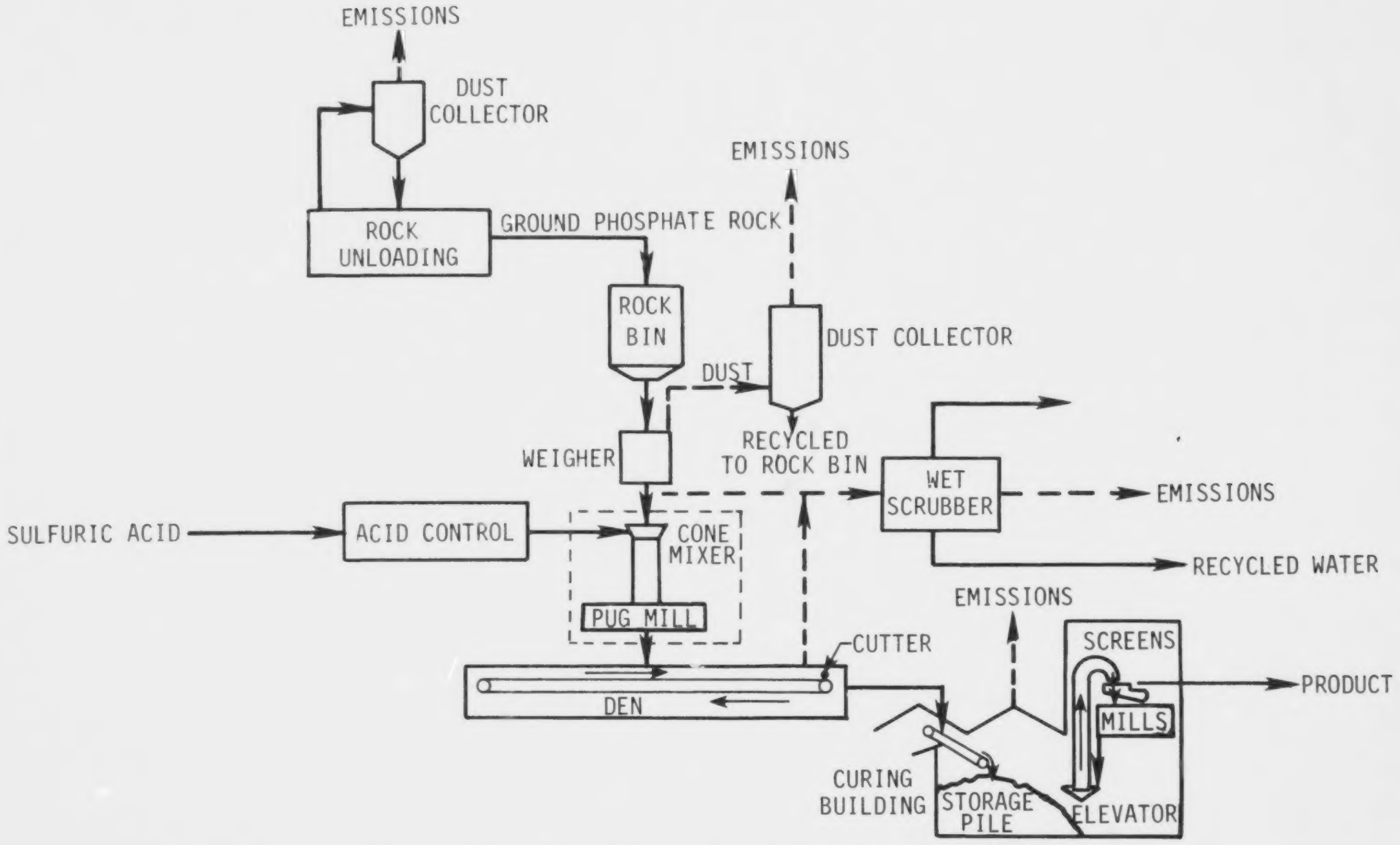
EMISSIONS
DUST COLLECTOR
ROCK UNLOADING
GROUND PHOSPHATE ROCK
EMISSIONS
ROCK BIN
DUST COLLECTOR
DUST
RECYCLED TO ROCK BIN
WEIGHER
WET SCRUBBER
EMISSIONS
SULFURIC ACID
ACID CONTROL
CONE MIXER
RECYCLED WATER
EMISSIONS
PUG MILL
CUTTER
SCREENS
DEN
PRODUCT
MILLS
CURING BUILDING
STORAGE PILE
ELEVATOR

Figure 4-6: Normal Superphosphate Process Flow Diagram

The GTSP process shown in Figure 4-7 is quite different. A lower concentration acid than that used in ROP is used for reaction with ground phosphate rock in an agitated tank. This lower strength acid maintains the resultant slurry in a fluid state and allows the chemical reaction to proceed further. Two methods, Dorr-Oliver and TVA, are used in GTSP production with the former (shown in Figure 4-6) accounting for over 30% of total production. A thin slurry obtained in this process is continuously removed and distributed onto dried granules to build up their size. Granulation is carried out in pug mills and rotating drums. Slurry-wetted granules are discharged onto a rotary dryer and are cooled before being sent for curing on a storage pile.

In the TVA granulation process, acidulation and granulation are carried out simultaneously in a rotary drum. Preheated acid, rock and recycled fines are mixed in the drum and granulated with steam. The product is cooled, screened and cured.

4.5.2 Emissions from TSP

The major sources of emission in an ROP-TSP plant are the mixer, den, curing building and gypsum pond. All sources release fluoride and particulates are released by all sources except the gypsum pond. Emissions of fluorides are controlled by wet scrubbers that discharge waste to the ponds. Table 4-5 shows emission factors for an average ROP-TSP plant based on source test data (3). An estimated 8 gF/kg P_2O_5 are released during production and curing of ROP-TSP. The emission points in GTSP plants are the reactor, granulator, dryer, cooler, screens, mills and storage. Again, most sources release fluorides and particulate. The dryer exhaust also contains SO_x from combustion of fuel oil.

Table 4-6 shows emission factors for a GTSP plant (3). Emissions from the reactor, granulator, dryer, cooler, screens and mills at an average plant are vented to a common stack. As a result Table 4-6 does not show individual emission factors. It is estimated that 7 gF/kg of GTSP are released during production and curing.

4.6 Summary of Fluoride Emissions

Table 4-7 summarizes the phosphate industry's fluoride emissions. It shows soluble fluoride evolution and emission associated with the 1970 and projected production levels. It should be noted that the emission factors of the individual processes include gypsum pond emissions (4).

4.7 References

1. Final Guideline Document: Control of Fluoride Emissions from Existing Phosphate Fertilizer Plants, EPA-450/2-77-005, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1977.

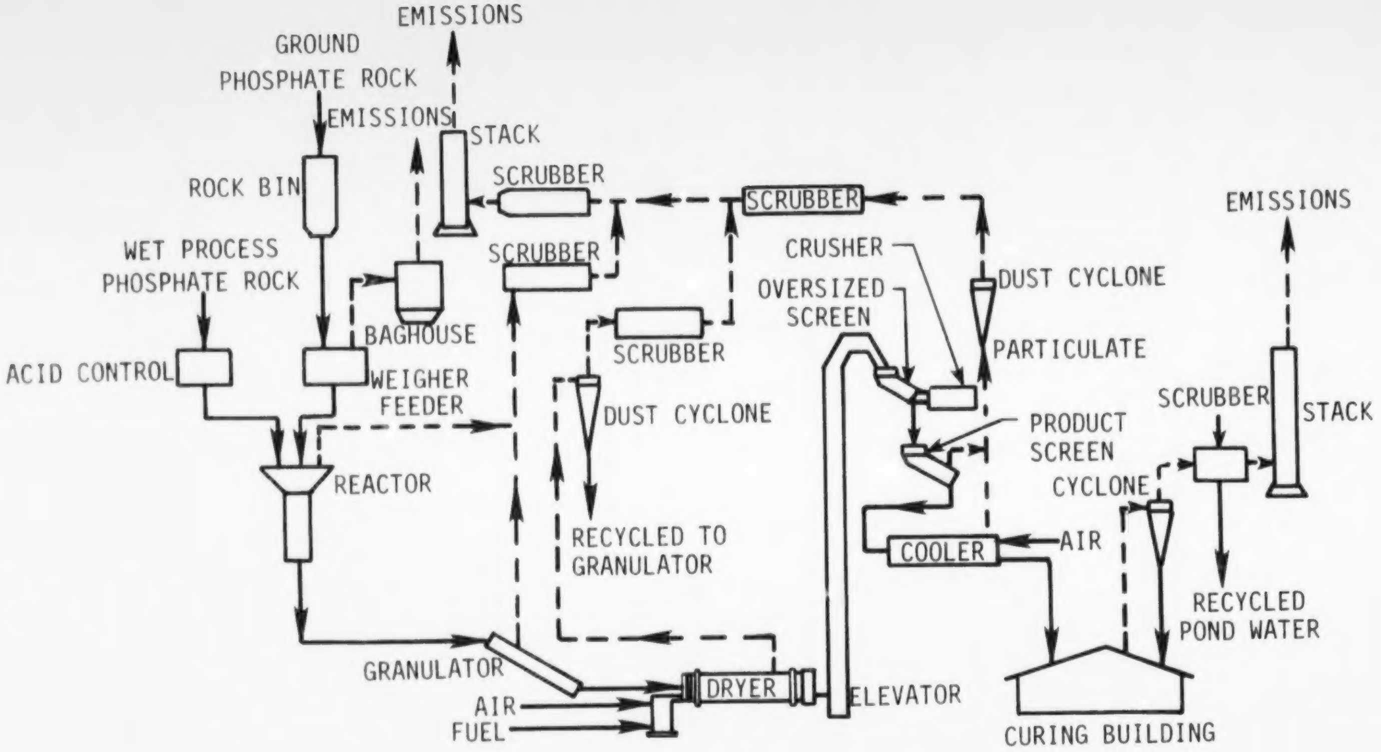
EMISSIONS
GROUND
PHOSPHATE ROCK
EMISSIONS
STACK
ROCK BIN
SCRUBBER
SCRUBBER
WET PROCESS
PHOSPHATE ROCK
SCRUBBER
BAGHOUSE
ACID CONTROL
WEIGHER
FEEDER
SCRUBBER
DUST CYCLONE
REACTOR
RECYCLED TO
GRANULATOR
GRANULATOR
AIR
FUEL
DRYER
ELEVATOR
CRUSHER
OVERSIZED
SCREEN
DUST CYCLONE
PARTICULATE
PRODUCT
SCREEN
COOLER
AIR
CYCLONE
EMISSIONS
SCRUBBER
STACK
RECYCLED
POND WATER
CURING BUILDING

Figure 4-7: Granular Triple Superphosphate Process Flow Diagram

TABLE 4-5. EMISSION FACTORS FOR AN AVERAGE RUN-OF-PILE TRIPLE SUPERPHOSPHATE PLANT BASED ON CONTROLLED EMISSION SOURCES (3)

Emission Source	Emission Factor, g/kg P_2O_5	
	Particulates	Fluorides[a]
Rock unloading	0.07[b]	–[c]
Rock feeding	0.014 ± 170%	–[c]
Cone mixer, den, curing building	0.16 ± 50%	0.10 ± 40%

---

[a] Fluoride released as a vapor.

[b] Based on two sets of data; therefore, 95% confidence limits could not be determined.

[c] Not emitted from this source.

TABLE 4-6. EMISSION FACTORS OF CONTROLLED EMISSIONS FOR AN AVERAGE GRANULAR TRIPLE SUPERPHOSPHATE PLANT (3)

Emission Source	Emission Factor, g/kg P_2O_5		
	Particulates	Fluorides	SO_x
Rock unloading	0.09[b]	–[c]	–[c]
Rock feeding	0.017 ± 180%	–[c]	–[c]
Reactor, granulator, dryer sooler, screens	0.05 ± 320%	0.12 ± 30%	1.86[b]
Curing building	0.10 ± 240%	0.018 ± 40%	–[c]

---

[a] Fluoride released as a vapor.

[b] Based on two sets of data; therefore, 95% confidence limits could not be meaningfully calculated.

[c] Not emitted from this source.

TABLE 4-7. PHOSPHATE INDUSTRIES FLUORIDE EMISSIONS (4)

	Wet Process Phosphoric Acid	Diammonium Phosphate	Triple Superphosphate	Normal Superphosphate	Electrothermal Phosphorus	Defluorination of Phosphate Rock	Industry Totals
1970 Production (10^6 tons/yr)	$3.8^{(B)}$	$2.4^{(B)}$	$1.4^{(B)}$	$0.7^{(B)}$	$1.6^{(A,D)}$	$0.09^{(A,\ )}$	$10.4^{(B)}$
Projected 2000 Production (10^6 tons/yr)	$13^{(B)}$	$7.0^{(B)}$	$2.7^{(B)}$	$0.2^{(B)}$	$2.6^{(A)}$	$0.14^{(A)}$	$26.3^{(B)}$
Soluble Fluoride Evolution Factor	$4.07^{(C)}$ lb F/ton P_2O_5 in Product	$1.31^{(C)}$ lb F/ton P_2O_5 in Product	$21.2^{(C)}$ lb F/ton P_2O_5 in Product	71 lb F/ton P_2O_5 in Product	30 lb F/ton P_2O_5 in Phosphate Rock Feed	$243^{(C)}$ lb F/ton P_2O_5 in Phosphate Rock Feed	16 to $9.3^{(C,E)}$ lb F/ton P_2O_5 Equiv. in Products
Soluble Fluoride Emission Factor with Current Control	$3.36^{(C)}$ lb F/ton P_2O_5 in Product	$0.23^{(C)}$ lb F/ton P_2O_5 in Product	$5.4^{(C)}$ lb F/ton P_2O_5 in Product	14.2 lb F/ton P_2O_5 in Product	5.1 lb F/ton P_2O_5 in Phosphate Rock Feed	$39^{(C)}$ lb F/ton P_2O_5 Phosphate Rock Feed	4.1 to $3.1^{(C,E)}$ lb F/ton P_2O_5 Equiv. in Products
Soluble Fluoride Emission Factor with 99% Control	$0.04^{(C)}$ lb F/ton P_2O_5 in Product	$0.013^{(C)}$ lb F/ton P_2O_5 in Product	$0.21^{(C)}$ lb F/ton P_2O_5 in Product	0.71 lb F/ton P_2O_5 in Product	0.30 lb F/ton P_2O_5 in Phosphate Rock Feed	2.4 lb F/ton P_2O_5 in Phosphate Rock Feed	$0.09^{(C)}$ lb F/ton P_2O_5 Equiv. in Products
Soluble Fluoride Evolved in 1970 (10^3 Tons F/year)	$7.73^{(C)}$	1.57	14.8	24.9	24.0	10.9	83.9
Soluble Fluoride Evolved in 2000 (10^3 tons/year)	$26.4^{(C)}$	4.59	28.6	7.10	39.0	17.0	123
Soluble Fluoride Emissions in 1970 (10^3 tons F/year)	$6.38^{(C)}$	$0.28^{(C)}$	$3.78^{(C)}$	4.97	4.08	$1.76^{(C)}$	21.3
Soluble Fluoride Emission in 2000 with Current Control (10^3 tons F/year)	$21.8^{(C)}$	$0.81^{(C)}$	$7.29^{(C)}$	1.42	6.63	$2.73^{(C)}$	40.7
Soluble Fluoride Emission in 2000 with 99% Control (10^3 tons F/year)	$0.26^{(C)}$	$0.046^{(C)}$	$0.28^{(C)}$	0.071	0.39	$0.17^{(C)}$	1.22

(A) Expressed as P_2O_5 equivalent in phosphate rock feed
(B) Expressed as P_2O_5 equivalent in product
(C) Includes gypsum pond emissions
(D) 1968 Data
(E) Reflects change due to shifts in production trends thru 2000.

2. Teller, A.J., Control of Gaseous Fluoride Emissions, Chemical Engineering Progress, 63:75-79, March 1967.

3. Nyers, J.M., et al, Source Assessment: Phosphate Fertilizer Industry, EPA-600/2-78-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1978, 184 pp.

4. Robinson, J.M., et al, Engineering and Cost Effectiveness Study of Fluoride Emissions Control, PB 207-506, prepared by TRW Systems Group for U.S. Environmental Protection Agency, January 1972.

5. Air Pollution Control Technology and Costs in Seven Selected Areas, EPA-450/3-73-010, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1973, pp. 11-192.

6. King, W.R., Ferrell, J.K., Fluoride Emissions from Phosphoric Acid Plant Gypsum Ponds, EPA-650/2-74-021, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1974, 329 pp.

7. Atmospheric Emissions from Wet-Process Phosphoric Acid Manufacture, AP-57 (PB 192 222), U.S. Department of Health, Education, and Welfare, Raleigh, North Carolina, April 1970, 86 pp.

8. Weber, W.C., Pratt, C.J., Wet Process Phosphoric Acid Manufacture In: Chemistry and Technology of Fertilizers, Sauchelli, V. (ed). New York, Reinhold Publishing Corporation, 1960, p. 224.

9. Riegel's Handbook of Industrial Chemistry, Seventh Edition, T.A. Kent, (ed). Van Nostrand Reinhold Co., New York, NY, 1974, pp. 551-569.

10. Inorganic Fertilizer Materials and Related Products, M 28B (75)-13, U.S. Department of Commerce, Washington, D.C., December 1976, 6 pp.

11. Shreve, R.N., Chemical Process Industries, Third Edition, McGraw-Hill Book Co., New York, NY, 1967, pp. 274-277.

12. Rawlings, G.D., Reznik, R.B., Source Assessment: Fertilizer Mixing Plants, EPA 600/2-76-032c, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1976, 187 pp.

5.0 STATE-OF-THE-ART AIR EMISSIONS CONTROL TECHNOLOGY

Phosphate fertilizer plants are rather unique in their air pollution control requirements. The air pollution control equipment cost for some processes may add up to over 50% of a plant's total capital investment. (In the words of one plant manager in central Florida, when building a fertilizer plant, first you erect the scrubbers and then you plan the rest of the equipment around them.) This section will first review the theory and practice of the wet scrubber, by far the most important control apparatus used in the fertilizer industry, and will then examine each of the five phosphate fertilizer processes for specific air pollution controls. A separate review of air pollution control equipment vendors will be presented in Section 8.

5.1 Theory and Practice of Wet Scrubbing

As can be seen in Section 4.0, the major air emissions from fertilizer plants consist of gaseous fluoride (primarily HF and SiF_4) and particulate matter. Air pollution control equipment can in general be divided into wet and dry cleaning devices. Dry gas cleaning devices, primarily represented by baghouses and electrostatic precipitators, are usually used in phosphate rock processing which is beyond the scope of work for this study. Phosphate fertilizer manufacturing processes start with phosphate rock acidulation which results in gaseous fluoride and particulate emission. Since wet scrubbers can simultaneously remove both emissions, their use in the fertilizer industry is widespread.

Wet scrubbers are air pollution control devices in which gaseous pollutants and/or aerosols are removed from the gas stream through scrubbing by a liquid. The wet scrubbers which are likely to perform well in phosphate fertilizer plants include spray towers, Venturi scrubbers, cross-flow packed scrubbers and impingement scrubbers. The physical and chemical phenomena by which contaminants are removed from the gas are called unit mechanisms and are somewhat different depending on whether gas or aerosol pollutants are involved.

Table 5-1 shows the advantages and disadvantages of wet scrubber devices.

5.1.1 Gaseous Fluoride Emissions Control

The basic unit mechanism for removal of a contaminant gas from the air is mass transfer, which can involve any or several of the transfer phenomena, such as molecular diffusion, turbulent diffusion, etc. The gas is transferred from one homogeneous phase (gas) to another (liquid). The driving force for this operation is concentration gradient. When mass transfer is in a direction from gas to liquid, the operation is called absorption; if the mass flows in the opposite direction, the operation is called desorption or stripping.

TABLE 5-1. ADVANTAGES AND DISADVANTAGES OF WET AIR AND GAS CLEANING DEVICES(1)

ADVANTAGES:

1. Gases and particles collected together.
2. Soluble materials may be readily collected and pumped.
3. High temperature gases cooled.
4. Corrosive gases and mists may be neutralized.
5. Fire or explosion hazard eliminated.

DISADVANTAGES:

1. May require recrystallization for soluble particles.
2. May require sludge pond.
3. Dissoluble particle recovery requires liquid filter.
4. Particles 1μm not easily collected.
5. Freezing problems.
6. Liquid entrainment in effluent frequent problem.
7. Cleaned air may not be suitable for recirculation, high dewpoint causes condensation.

The gas on its way from bulk gas to bulk liquid and to final elimination must overcome three resistances (2):

1. Diffusion through a gas phase film
2. Diffusion through a liquid phase film
3. Chemical reaction rate.

Any one or a combination of the three resistances can be the rate controlling step.

The rate of mass transfer N_A is:

$$N_A = K_G (P_G - P_i) = K_L (Ci - C_L)$$

where

N_A = mass transfer

K_G = gas film mass transfer coefficient

K_L = liquid film mass transfer coefficient

$P_{G,i}$ = pressure, G-gas, i-interphase

$C_{i,L}$ = concentration, i-interphase, L-liquid

The experimental determination of the individual coefficients K_G and K_L is difficult. When the equilibrium line is straight, overall coefficients similar to those used in heat transfer can be used and they can be defined from the standpoint of either the gas or liquid phase. Each coefficient is based on a calculated overall driving force.

One of the most important engineering parameters in the design of a wet packed scrubber is the height of the packed section. A useful method for computing the height of a packed tower is based on the transfer unit concept (3). The physical meaning of a transfer unit is that it is a section of a packed tower that achieves a change in composition equal to the driving force in that section (4). The advantage of this method is that it is much simpler than the use of mass transfer coefficients.

In the case of packed towers which are frequently used in phosphate fertilizer plants, the following mass transfer relationships have been established:

$$K_G \sim G^{0.8}$$

where:

K_G = mass transfer coefficient, Kg moles/hr, m^3, atm

G = gas mass flow rate, Kg moles/hr m^2

Therefore:

$$N_T \sim \frac{Z}{G^{0.2}}$$

N_T = number of transfer units

Z = tower height, m

Thus, the number of transfer units obtainable would be controlled by the height of the tower, but the number of transfer units usually also increases as the liquid mass flow rate is increased.

Table 5-2 shows HF absorption data for various wet scrubbers (5). These scrubbers will be described in more detail in Section 5-2.

An important consideration in gaseous pollutant removal is the performance of equipment. It is sometimes difficult to compare the performance of two basically different types of equipment in terms of mass flow rates, height of transfer unit, or mass transfer coefficients. In order to overcome this difficulty, the performance of equipment has been studied in terms of the number of transfer units. The effect of liquid and gas flow rates is also expressed in terms of theoretical power consumed per unit of gas flow rate, as power consumption is usually of more economic concern than liquid or gas mass flow rate. Such relationships are mainly a matter of convenience and do not necessarily have a theoretical basis.

Figures 5-1 and 5-2 show the relationship between number of transfer units and power consumption in absorption of HF and SiF_4. It has been shown that the number of transfer units obtainable on grid towers is controlled principally by tower height and is only slightly affected by power expended on the liquid and gas phases. The performance of cyclone spray scrubbers is primarily a function of power expended in the liquid phase and is essentially independent of the power expenditure in the gas phase. Performance of Venturi scrubbers, on the other hand, depends largely on the power expended in the gas phase but is slightly affected by liquid power expenditure. These results are useful in characterizing the dominant factors in the performance of equipment used in the absorption of gaseous fluorides.

Nearly all usable data from the absorption of hydrogen fluoride are based upon application of spray towers. The performance of this equipment appears to be dominated by the power expended on the liquid phase, as was the case with the cyclone scrubber. Significant differences in performance among the various spray towers in use were found. Wet-cell washers require a higher power consumption than simple spray towers with the same performance.

TABLE 5-2. HYDROGEN FLUORIDE ABSORPORATION DATA (5)

Type of Equipment	Absorbing Liquor	G, Lb/(Hr) (Sq. Ft.)	L, Lb/(Hr) (Sq. Ft.)	Pg, Hp., /M Cu. Feet/Min	Pt, Hp., /M Cu. Feet/Min	Kga Lb. Mole (Hr) (Cu. Ft.) (Atm.)	Nr
Cross flow spray	Water	2,110	72	~0.0067	0.0089	~11	~0.33
		1,880	72	~0.0056	0.0098	~12	~0.38
		2,080	103	~0.0067	0.0067	~12	~0.25
		1,830	84	~0.0067	0.017	~15	~0.62
		1,400	92	~0.0061	0.017	~25	~1.09
Cross flow spray	Lime water	2,050	105	~0.006	0.013	~35	~1.50
Counterflow spray	Water	2,000	800	~0.2	0.10	9	~5.85
Parallel flow spray	Lime water	13,800	3,800	~0.23	0.017	51	2.58
Counterflow spray	Water	2,000	380	0.24	0.02	4	2.5
Venturi	Water	76,000	42,000	4.7	0.071	-	2.9
Venturi	Water	~70,000	~40,000	2.1	0.074	-	2.0
			65,000				
				2.4	0.11	-	2.7
				2.9	0.071	-	2.3
				3.5	0.095	-	3.0
				4.0	0.12	-	3.9
				4.5	0.13	-	2.3

G = Gas mass flow rate
L = Liquid mass flow rate
Pg = Power in gas phase
Pl = Power in liquid phase
Kga = Mass transfer coefficient
Nt = Number of transfer units

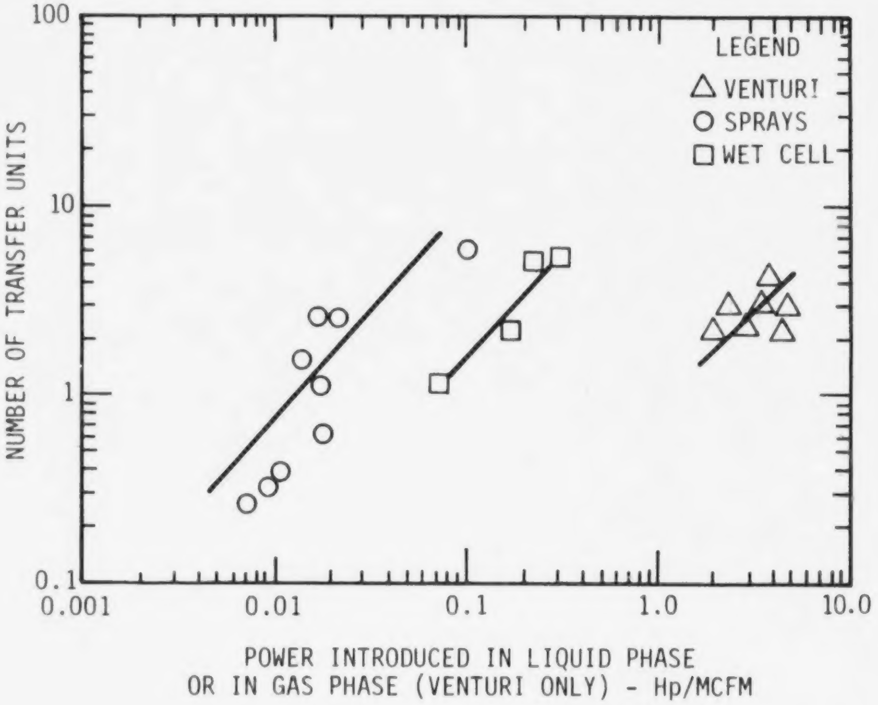

Figure 5-1: Power Consumed in HF Absorption (5)

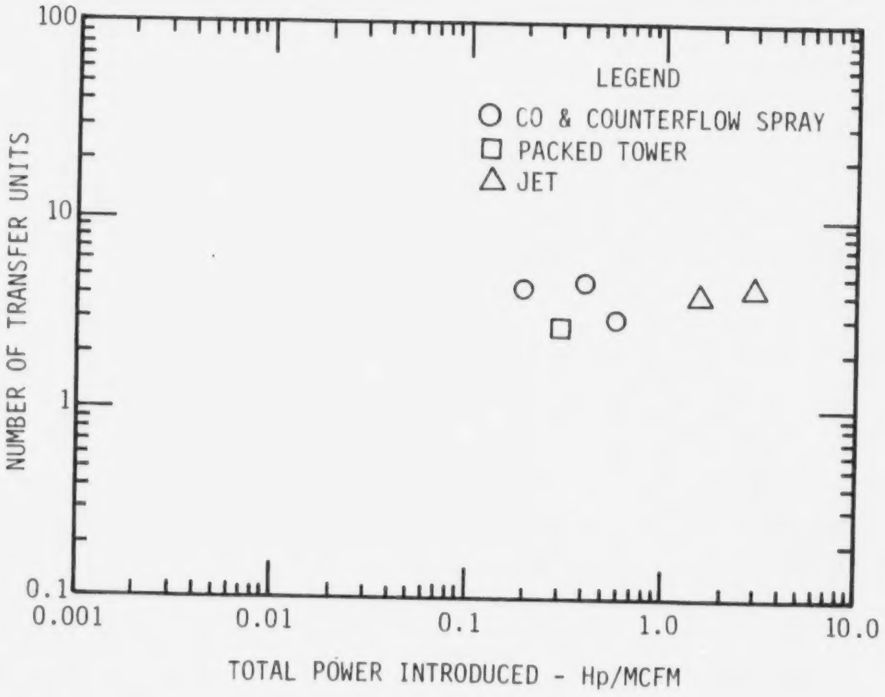

Figure 5-2: Power Consumed in SiF Absorption (5)

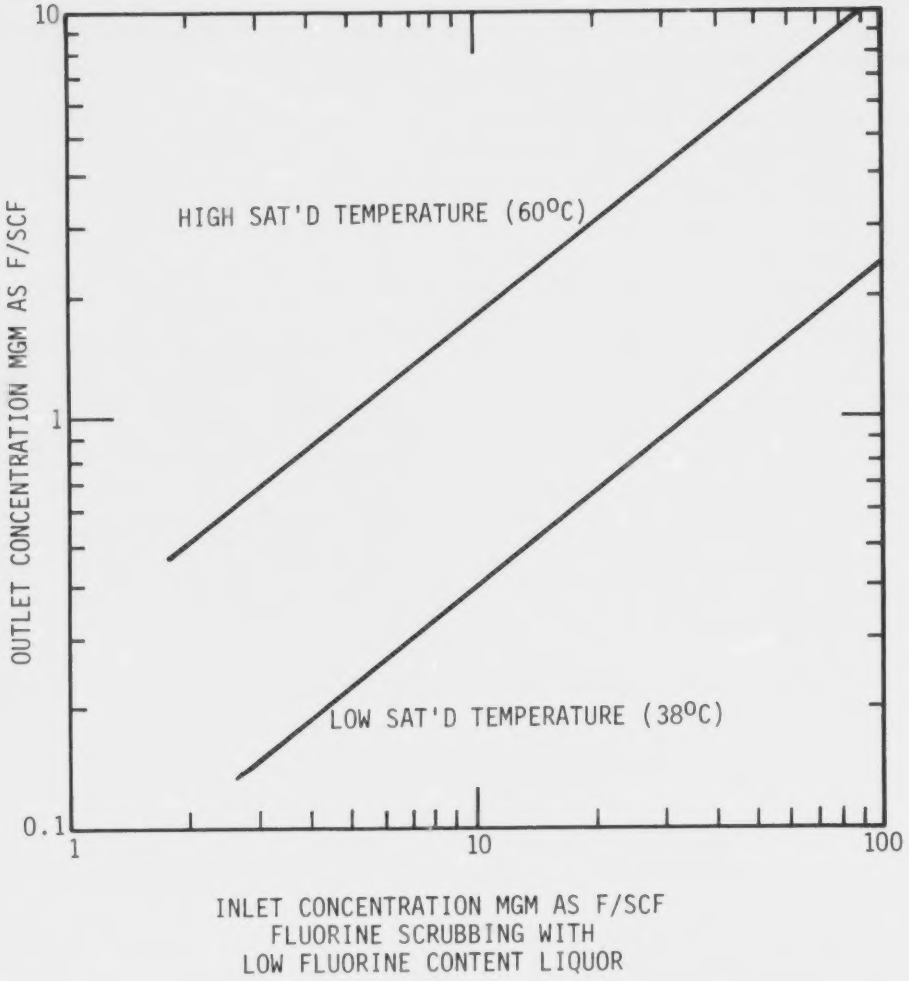

Figure 5-3: Inlet Versus Outlet Fluoride Concentration in Cyclonic Spray Tower (6)

The performance of spray towers absorbing silicon tetrafluoride is not consistent with simple gas absorption. One possible explanation is that mists are formed in the tower, which are collected primarily in the entrainment separators just prior to emergence from the tower. The mist is probably rather coarse, however, because high-power consuming devices such as jet scrubbers do not exhibit substantially better performance than the low-power-consuming spray towers.

In general, the extent of the fluorine abatement system required is determined by the following parameters:

1. the inlet fluorine concentration,
2. the allowable fluorine emissions,
3. the outlet or saturated gas temperature,
4. the composition and temperature of the scrubbing liquid,
5. the scrubber effectiveness and number of transfer units,
6. the fluorine compounds present, and
7. the effectiveness of entrainment separation.

The inlet and allowable outlet fluorine concentrations must first be established to determine the overall scrubbing requirement. Figure 5-3 shows the relationship between saturated gas temperatures and the overall removal efficiency of a cyclonic spray tower scrubber (6). The gas streams leaving the scrubber are saturated with water vapor. When the scrubber is operated at a relatively low saturated temperature (gas temperature close to pond water temperature), the efficiency is high. Since absorption decreases with temperature increase, efficiency is lower at a higher saturated temperature. An additional advantage of scrubber operation is that silica is kept in a gelatinous stage which is easily washed from the scrubbing device. At higher temperatures, the silica is crystallized on the scrubber and removed with great difficulty.

The scrubber effectiveness, or the number of transfer units, will determine the overall scrubbing requirements.

Transfer units are defined by the following formula:

$$\mathrm{NTU} = \ln \frac{\text{Inlet F}}{\text{Outlet F} + a}$$

where "a" is the vapor pressure contribution of fluorine from the scrubbing media. Once the overall transfer unit requirements are determined, the number of scrubbing stages may then be set based upon the performance of each scrubbing device employed.

The information included in Table 5-2 and Figures 5-1, 5-2, and 5-3 is typical of the information necessary for scrubber design.

5.1.2 Particulate Emissions Control

Various types of wet scrubbers are used for removal of particulate matter* emanating from phosphate fertilizer processes. The principle of particle collection in wet scrubbers is based on bringing the particle close to the collecting bodies (liquid droplets) whereupon a number of short range mechanisms accomplish the actual collection. The basic unit mechanisms for aerosol collection are:

1. Inertial impaction
2. Interception
3. Diffusion

In some special circumstances, other mechanisms involving forces such as electrostatic, thermal, magnetic, etc., may play an important role. Fortunately, in most cases one mechanism predominates so that the problem can be dealt with on a theoretical basis.

Analysis of the principle of aerosol collection in wet scrubbers should start with analysis of the flow of air around a spherical droplet. Throughout this analysis, one should keep in mind that similar collection principles apply to dry filtration with the exception that the collecting body is not a sphere but a cylinder (filter fiber). In cases where a packed tower is used for aerosol collection, the collecting body can be approximated by a flat plate. Aerosol collection can be best illustrated by the example of the Venturi scrubber. The stream of gas containing particulate matter is accelerated in the Venturi throat. The scrubbing liquid is injected into the throat forming droplets which capture aerosol particles via unit mechanisms. The analysis may be reduced to viewing two elements: one is stationary (liquid droplet) and the other (aerosol particle) is immersed in gas moving toward the droplet. The gas streamlines will follow the surface of the liquid droplet, while the aerosol particles, because of their larger mass (compared with air molecules), will have sufficient momentum to continue to move toward the liquid droplet, will break through the gas streamlines, and become trapped in the droplet. The unit mechanism is referred to as inertial impaction.

Three factors determine the efficiency of inertial impaction:

1. Velocity distribution of the gas flowing by the droplet which varies with Reynolds Number.

2. Particle trajectory which depends on mass and size and shape of the aerosol particle and the size of the droplets, and the rate of flow of the gas stream.

3. Adhesion of particles to droplets (usually assumed to be 100%-this is questioned by some researchers when the aerosol is hydrophobic).

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*The terms "particulate matter" and "aerosol" are used interchangeably in this discussion.

Using the equation describing the motion of particles and assuming that the particles obey Stokes' Law, a parameter of inertial impaction has been derived(7).

$$\psi = \frac{c\rho V_o D_n^2}{18\mu D_c}$$

where:

ψ = inertial impaction parameter (dimensionless)

c = Cunningham empirical correction factor (dimensionless)

ρ = particle density, gram mass per cc

V_o = initial (undisturbed) velocity of aerosol stream, cm per second

D_n = diameter of aerosol particle, cm

D_c = diameter of liquid drop, cm

μ = gas velocity, poise

The physical significance of the inertial impaction parameter is that it is the ratio of the force necessary to stop a particle initially travelling at velocity Vo in the distance Dc/2 to the fluid resistance at a relative particle velocity of Vo. It is also a ratio of stopping distance to collector diameter (droplet) (8).

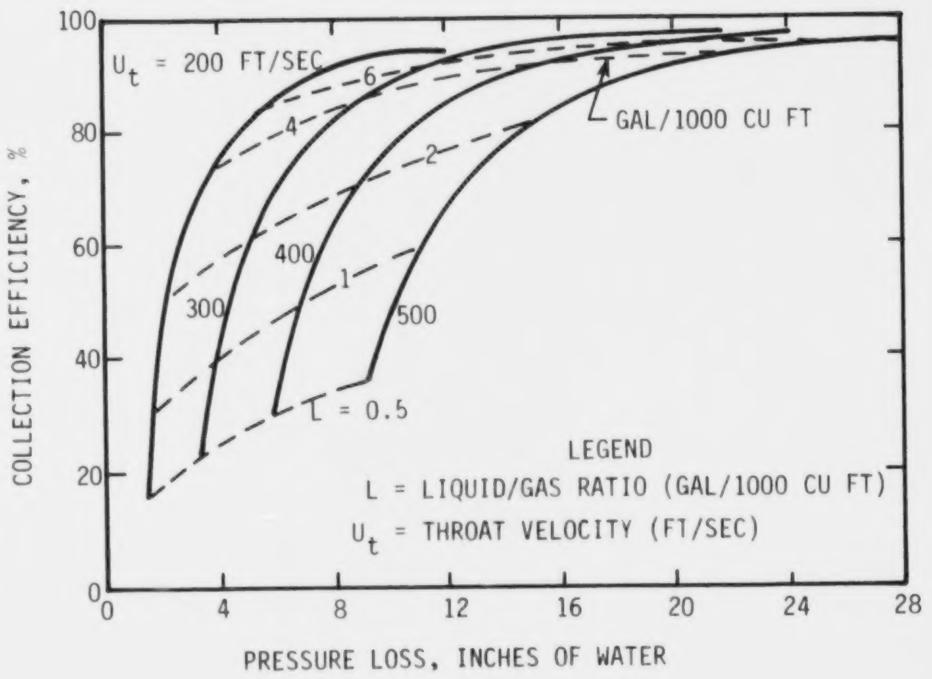
The importance of the other basic unit mechanisms on particulate removal in the phosphate fertilizer industry is negligible and will not be discussed here. For a detailed description of the theory and practice of wet scrubbing, refer to the Scrubber Handbook (9).

The overall efficiency of aerosol collection in wet scrubbers is the function of several parameters. Major influences on collection efficiency are:

1. Aerosol size: The larger the size, the higher the aerosol collection efficiency. The size with a minimum collection is in a range from 0.1 - 0.8 microns.

2. Pressure drop: The higher the pressure drop, the higher the aerosol collection efficiency as long as inertial impaction with interception is the mechanism of collection (see Figure 5-4 (10)).

3. Liquid to gas ratio: There appears to be an optimum liquid to gas ratio. The size, number, and distribution of liquid droplets generated in the Venturi throat is usually calculated using the Nukiyama-Tanasawa equation (11).



Fiugre 5-4: Venturi Scrubber Performance (10)

Other factors of importance include: wettability of the aerosol particles, ratio of aerosol to drop sizes, and physical properties of the scrubbing liquid.

It has also been demonstrated that the efficiency of a Venturi scrubber can be increased by lowering the surface tensions and viscosity of the scrubbing liquid (12).

In an article on equipment performance in controlling fluoride emissions, Lund (5) stresses the difficulty of evaluating wet scrubbers for particulate removal:

> The evaluation of liquid scrubbing devices with regard to the collection of particulate fluorides is far more difficult than with regard to absorption of gaseous fluorides. The predominant factor controlling the rate of collection of particulate matter is effective particle size. No data have been published on the particle size or size distribution of particulate fluoride emissions from industrial processes (5).

Lapple and Kamack (13) have shown that within wide limits power consumption is a key criterion in particulate emission control efficiency. The power can be introduced either in a liquid or gas phase so that scrubber design specifics play a minor role. This finding was also confirmed by other investigators, leading to serious questions as to whether one scrubber configuration is really superior to another at the same power consumption.

Depending on the size of the particulate fluorides, the power consumption for efficient collection may be no more than that for the absorption of gaseous fluorides, or it may be vastly greater. When a scrubber is used for simultaneous removal of gaseous and particulate fluorides, the power requirements for the latter frequently become the dominating factor.

Although there are a number of large control installations in the phosphate fertilizer industry for the removal of gaseous fluoride and particulate, little information has been published on equipment performance and power consumption.

TRC will recommend two studies to fill in this gap in information. The first study is on the optimization of scrubbers through factorial design experiments; the second is the evaluation of the potential for energy conservation in phosphate fertilizer plants. The reasons, objectives and scope of work for these studies are presented in Section 9.

The next section will briefly describe the scrubbers most frequently used in the phosphate fertilizer industry.

5.2 Types of Scrubbers Used in Phosphate Fertilizer Plants

5.2.1 Cyclonic Spray Scrubber

Spray towers provide the contact necessary for gas absorption by dispersing the scrubbing liquid in the gas phase in the form of a fine spray. Cyclonic spray towers eliminate excessive entrainment of scrubbing liquid by utilizing centrifugal force to remove entrained droplets. Figure 5-5 is a schematic diagram of a typical spray tower. A tangential inlet is used to impart the spinning motion to the gas stream which flows parallel to the water sprays. Pressure drops across the scrubber range from 2-8 inches of water. Although solids handling capacity is high, absorption capacity is limited to about two transfer units (14).

5.2.2 Venturi Scrubbers

The Venturi scrubber provides a high degree of gas-liquid mixing but the relatively short contact time limits its absorption capabilities, so it is primarily used for particulate removal. Two types of Venturi scrubbers, gas-actuated and water-actuated, shown in Figures 5-6 and 5-7 (15), are in general use. The necessary gas-liquid contact is obtained from the velocity difference between the two phases and turbulence in the Venturi throat. Both types also require the use of mist eliminators for removal of entrained scrubbing liquid.

The gas-actuated Venturi uses the velocity of the gas stream as the energy required for liquid atomization and consequent gas-liquid contact. The water-actuated Venturi uses the velocity of the water stream as the source of energy. The gas-actuated Venturi normally operates at a pressure drop of 8-20 inches of water while the water-actuated develops up to 8 inches at high liquid flow rates (16). The water-actuated Venturi is limited to gas flow rates up to approximately 5,000 CFM.

5.2.3 Spray-Crossflow Packed Scrubber (SCFS)

The spray-crossflow packed bed scrubber has been accepted as the most satisfactory fluoride control device available for wet process phosphoric acid plants. Recent improvements in spray-crossflow packed scrubber designs have alleviated the initial problem of plugging and allow a greater solids handling capacity.

As shown in Figure 5-8, the spray-crossflow packed bed scrubber consists of two sections, a spray chamber and a packed bed, separated by a series of irrigated baffles. Both sections are equipped with gas inlets. Effluents with high fluoride and particularly high SiF_4 concentrations are treated in the spray chamber before entering the packing. This reduces the danger of plugging in the bed, reduces the loading on the packed stage, and provides some solids handling capacity. The crossflow design operates with the gas stream moving horizontally through the bed with the scrubbing liquid flowing vertically through the packing. Solids deposited near the front of the bed are washed off by a cleaning spray. Pressure losses through the scrubber range from 1-8 inches of water, the average being about five inches.

Recycled gypsum pond water is normally used as the scrubbing liquid in both the spray and packed sections.

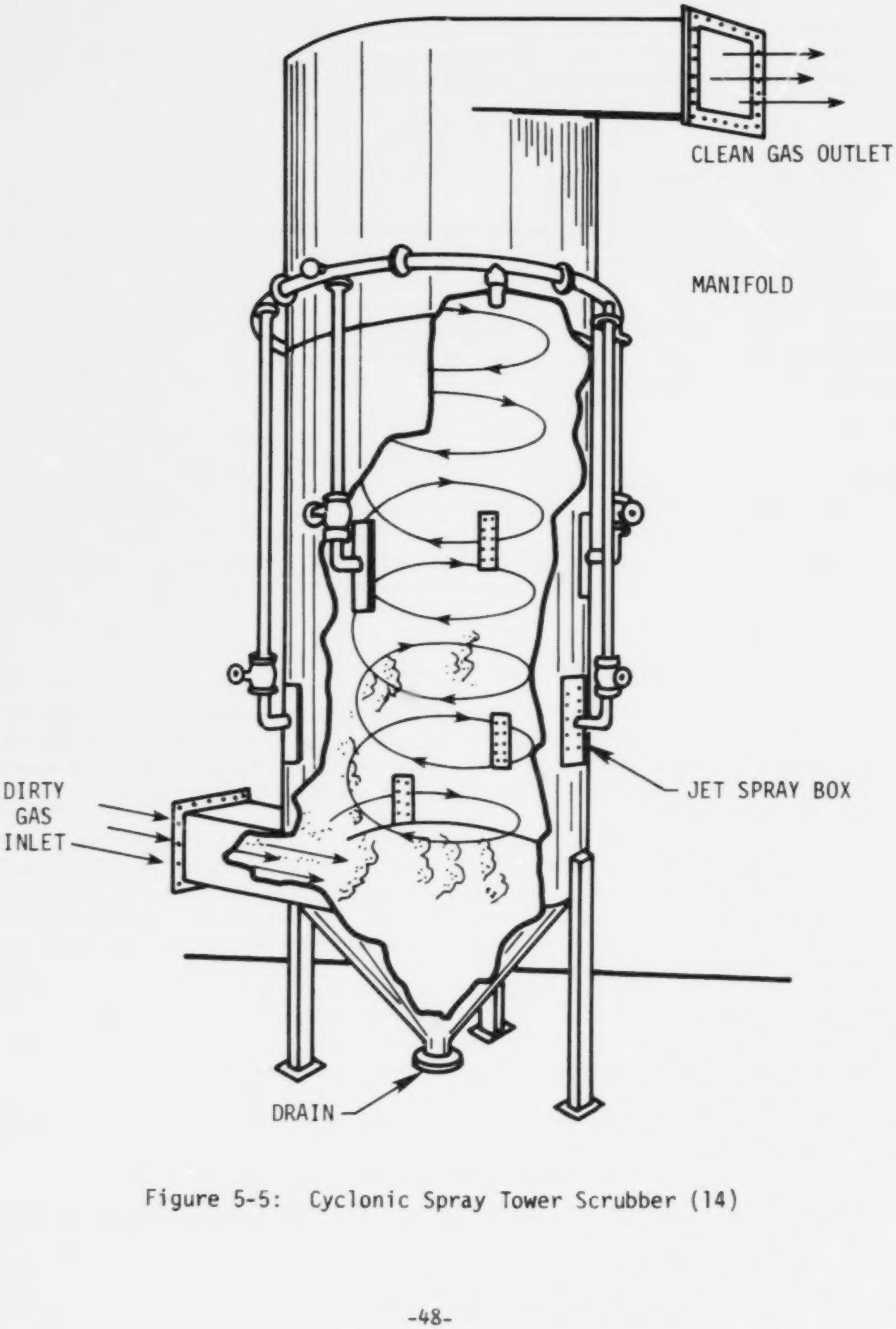

CLEAN GAS OUTLET
MANIFOLD
JET SPRAY BOX
DIRTY GAS INLET
DRAIN

Figure 5-5: Cyclonic Spray Tower Scrubber (14)

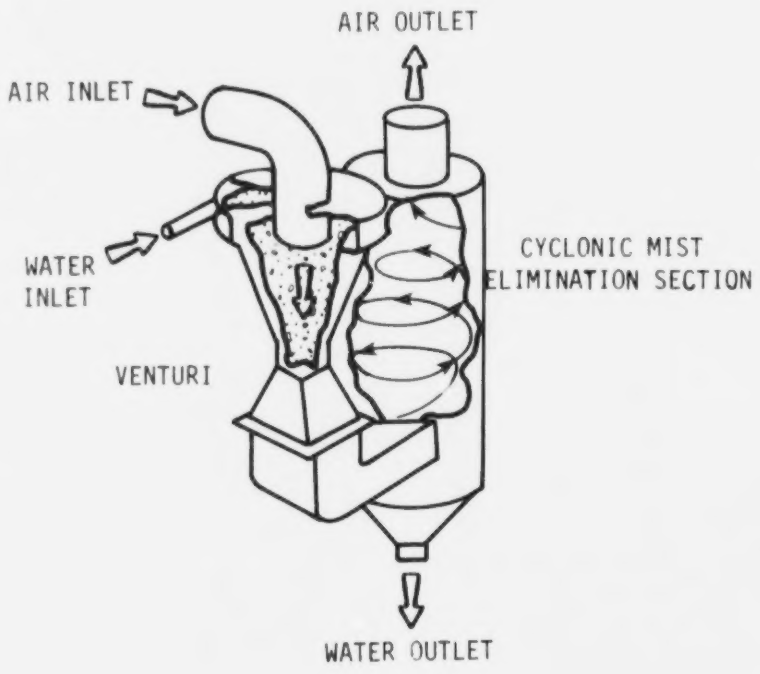

AIR OUTLET
AIR INLET
WATER INLET
CYCLONIC MIST ELIMINATION SECTION
VENTURI
WATER OUTLET

Figure 5-6: Gas-actuated Venturi Scrubber With Cyclonic Mist Eliminator (15)

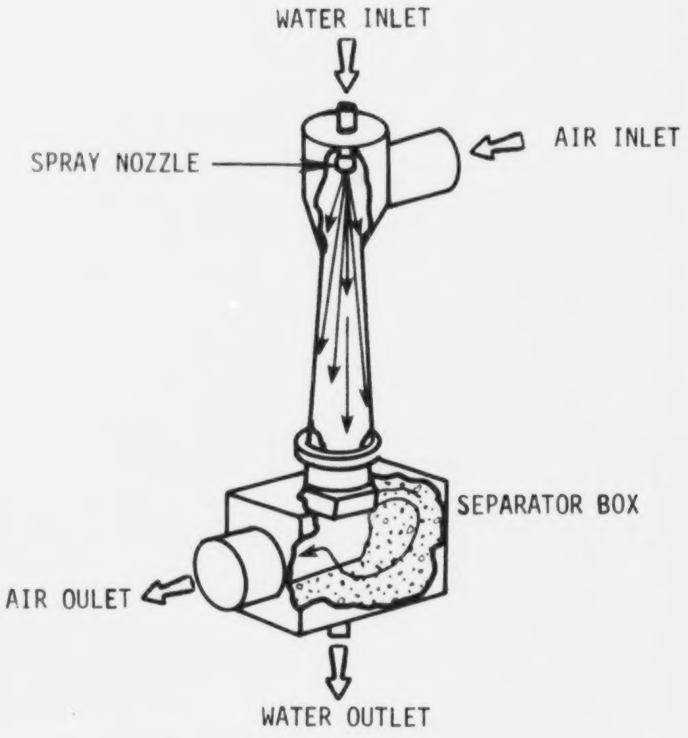

WATER INLET
SPRAY NOZZLE
AIR INLET
SEPARATOR BOX
AIR OULET
WATER OUTLET

Figure 5-7: Water-actuated Venturi (15)

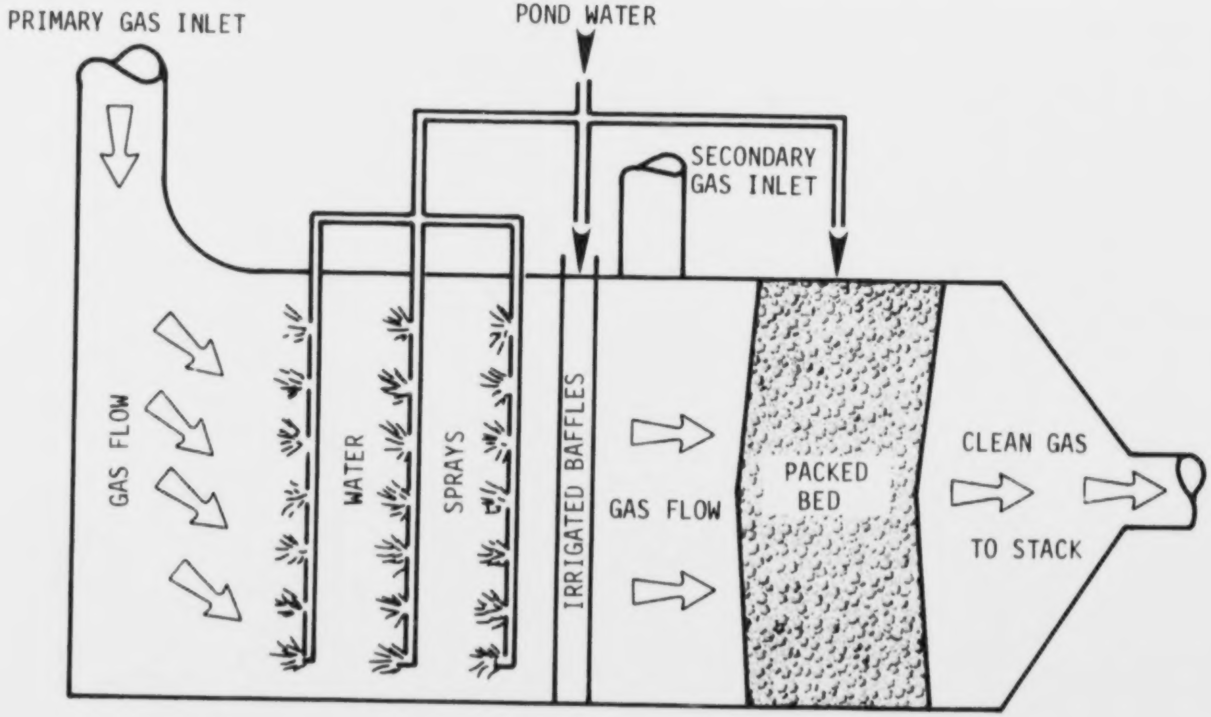

PRIMARY GAS INLET
POND WATER
SECONDARY GAS INLET
GAS FLOW
WATER
SPRAYS
IRRIGATED BAFFLES
GAS FLOW
PACKED BED
CLEAN GAS
TO STACK

Figure 5-8: Spray-Crossflow Packed Bed Scrubber (14)

5.2.4 Coaxial Scrubber

The major objective of the coaxial scrubber and similar devices is to minimize deposition of solids. An example of the coaxial design as manufactured by Teller Environmental Systems, Inc. (TESI) is shown in Figure 5-9. This TESI scrubber is used primarily for ammonia absorption with phosphoric acid.

The liquid flow rate is linear, requiring no turns. Thus, the liquid is not subjected to mechanical shock that could result in deposition of solids. Liquid distribution is primarily achieved by underflow weirs. The Venturi throat is of a diamond design to minimize scale-up. The design of the coaxial scrubber is said to be such that the definition of flow patterns is far more precise than that in cyclones of the same diameter resulting in higher efficiency (17).

The next sections will present the state-of-the-art in air emission control technology in the phosphate fertilizer industry. Special emphasis will be on the equipment cost.

5.3 Wet Process Phosphoric Acid (WPPA)

The present emission guideline for wet process phosphoric acid plants limits fluoride emissions to 0.01 grams of fluoride (as F^-) per kilogram of P_2O_5 input to the process. This emission guideline is equal to the standard of performance for new plants and requires removal of 99% of emitted fluoride. A spray-crossflow packed bed scrubber installed in 53% of the WPPA plants (accounting for 74% of the total production capacity) can achieve this requirement.

Figure 5-10 shows the emission streams and crossflow scrubber in a typical WPPA plant. The scrubber consists of two sections--a spray chamber and a packed bed--separated by a series of irrigated baffles. A typical unit treating the effluent streams from a wet acid plant (20,000 SCFM) is 9 feet wide, 10 feet high and 30 feet long (18). The packed bed is usually 3 or 4 feet in length, while the pressure drop through the unit averages 4-6 inches of water. Recycled pond water is normally used as the scrubbing liquid in both the spray and packed section. The ratio of scrubbing liquid to gas ranges from 0.02 to 0.07 gpm/acfm.

Table 5-3 shows EPA data on crossflow scrubber performance in WPPA plants.

In 1973 the Industrial Gas Cleaning Institute (IGCI), under contract to EPA, prepared the specifications for a scrubbing system for WPPA using pond water (20). Table 5-4 shows the operating condition for a scrubber which was to be manufactured from PVC, rubber-lined steel, or FRP. Table 5-5 shows average capital and annual cost obtained from several equipment vendors. It should be noted that these costs represent 1973 figures. In order to bring the costs up to date one can use economic indicators from Chemical Engineering (21). From the latest available CE plant cost index (based on 1957-1959 = 100) for September 1978, an average correction index of 179 can be derived. Consequently, today's projected total

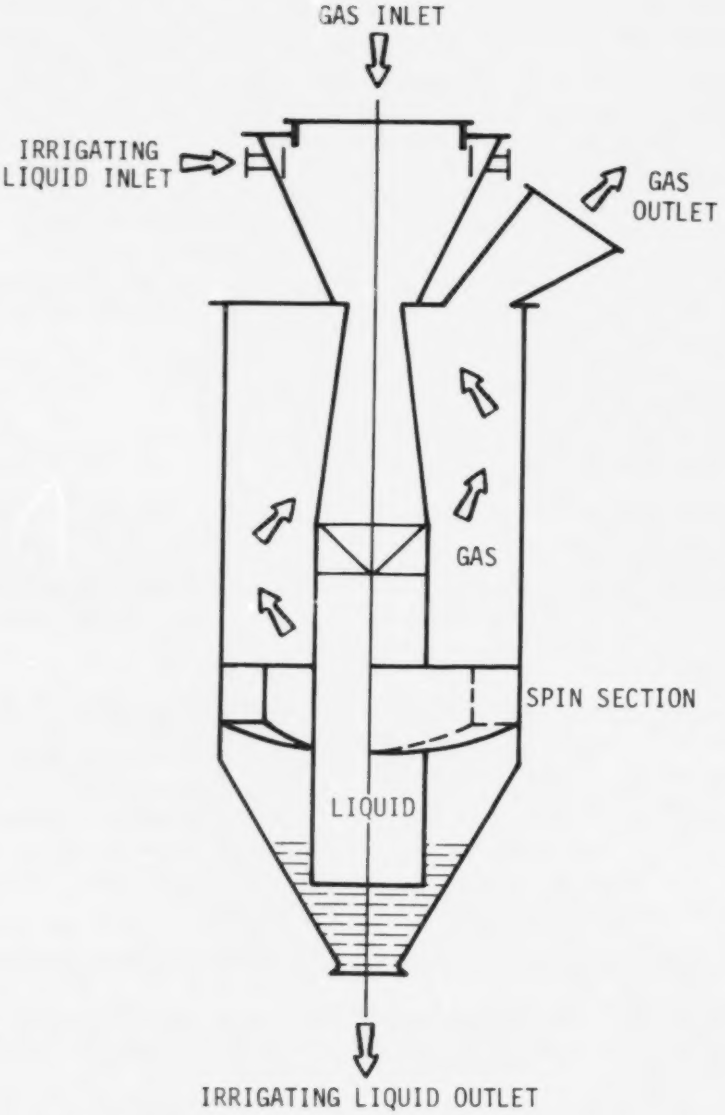

GAS INLET
IRRIGATING LIQUID INLET
GAS OUTLET
GAS
SPIN SECTION
LIQUID
IRRIGATING LIQUID OUTLET

Figure 5-9: Teller Coaxial Scrubber (17)

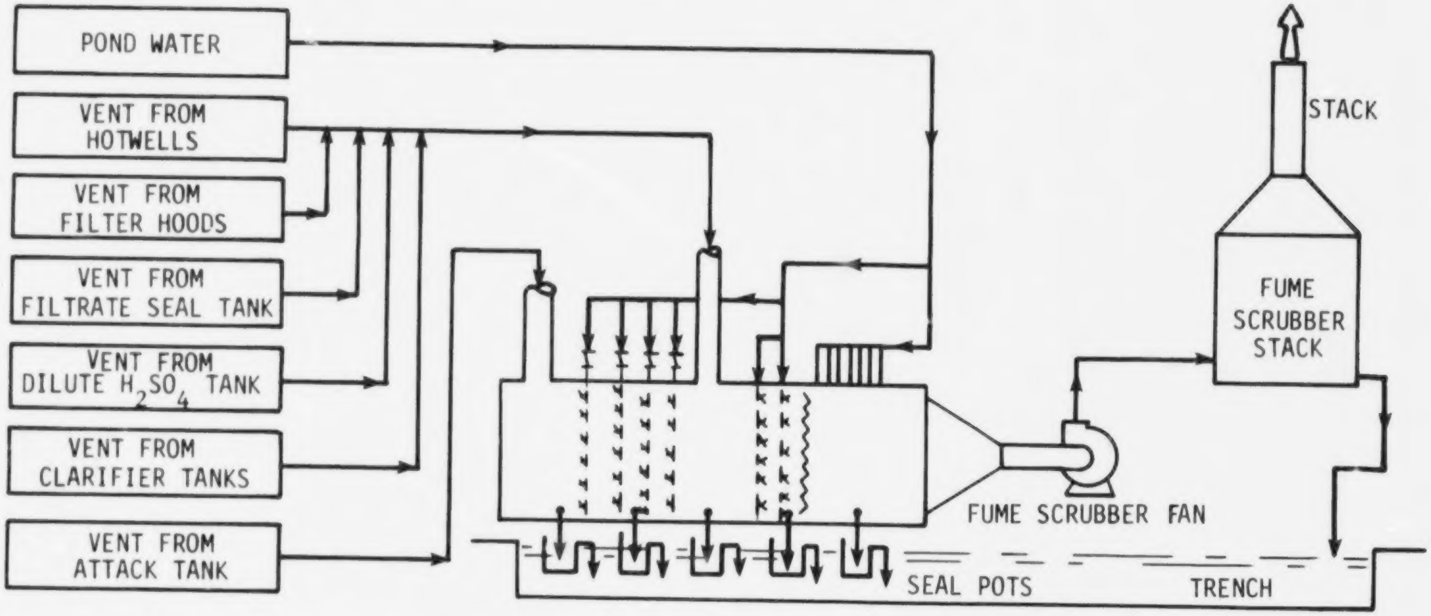

POND WATER
VENT FROM HOTWELLS
VENT FROM FILTER HOODS
VENT FROM FILTRATE SEAL TANK
VENT FROM DILUTE H_2SO_4 TANK
VENT FROM CLARIFIER TANKS
VENT FROM ATTACK TANK
STACK
FUME SCRUBBER STACK
FUME SCRUBBER FAN
SEAL POTS
TRENCH

Figure 5-10: Spray-Crossflow Packed Bed Scrubber in Wet Process Phosphoric Acid Plant

TABLE 5-3. SCRUBBER PERFORMANCE IN WET-PROCESS PHOSPHORIC ACID PLANTS (19)

Plant	Scrubber Design	Fluoride Emissions[a] (lb F/ton P_2O_5)
A	Spray-cocurrent packed bed	0.015
B	Spray-crossflow packed bed	0.006
C	Spray-crossflow packed bed	0.002, 0.012[b]
D	Spray-crossflow packed bed	0.011

[a] Average of testing results.

[b] Second series of tests.

TABLE 5-4. OPERATING CONDITIONS FOR WET PROCESS PHOSPHORIC ACID PLANT CROSS-FLOW PACKED SCRUBBER (20)

	SMALL	LARGE
Plant Capacity, Ton/Day P_2O_5	500	900
Acid Strength, Wt. % P_2O_5:		
From Digesters	30	30
From Evaporators	54	54
Fluorine Content, Wt. % F	1.5	1.5
	B	D
Gas to Scrubbers:		
Flow, SCFM	25,000	36,000
Flow, DSCFM	21,050	30,300
Flow, ACFM	28,300	40,600
Temp., °F	140	140
Moisture, Vol. %	15.7	15.7
Fluorine, lb/hr	80	115
Fluorine, ppm	1,050	1,050
Particulate, lb/hr	10.8	15.5
Particulate, gr/SCF	0.05	0.05
Gas from Scrubbers:		
Flow, SCFM	22,600	32,500
Flow, DSCFM	21,050	30,300
Flow, ACFM	23,700	34,400
Temp. °F	100	100
Moisture, Vol. %	6.7	6.7
Fluorine, lb/hr	0.16	0.29
Fluorine, ppm	2.35	2.95
Fluorine Removal, Wt. %	99.80	99.75
Particulate, lb/hr	0.07	1.4
Particulate, gr/SCF	0.05	0.005
Particulate Removal, Wt. %	91.1	91.1
Estimated y', ppm	1.4	1.4
Estimated NTU required	7.5	6.50

TABLE 5-5. CAPITAL AND ANNUAL COST FOR CFPS ON WPPA PLANTS (19)
(1974 COSTS)

Plant Size TPD P_2O_5	500	900
Gas Flow SCFM	25,000	36,000
Capital Cost ($)		
Scrubber	17,700	21,600
Auxiliary equipment (fan, pumps, etc.)	8,500	9,400
Installation cost	36,300	40,900
Total Capital Cost	62,500	71,900
Annual Cost ($/yr)		
Operating labor	2,000	2,000
Maintenance (5%)	3,100	3,600
Utilities	2,800	4,400
Depreciation (10 yr)	6,250	7,200
Interest (8%)	5,000	5,750
Property Tax, Ins. (2%)	1,250	1,450
Administrative (5%)	3,100	3,600
Total Annual Cost	23,500	28,000

control cost for a 25,000 ACFM installation is \$112,000 and for a 36,000 SCFM, \$129,000.

As mentioned previously, most plants today use spray-crossflow scrubbers and can meet current regulations. The rest of the plants use spray scrubbers which will have to be retrofitted with SCFS to be in compliance. Table 5-6 shows the cost associated with retrofitting a WPPA plant that uses a spray tower with SCFS.

5.4 Superphosphoric Acid (SPA)

The present emission guideline for SPA plants limits fluoride emissions to 0.005 grams of fluoride (as F^-) per kilogram of P_2O_5 input to the process. This emission guideline is equal to the standard of performance for new plants (NSPS) and would require approximately 50% removal. A spray-crossflow scrubber is capable of providing this performance (16). Plants using the vacuum evaporation process (79% of the SPA industry) will require no additional control.

Figure 5-11 shows a spray-crossflow scrubber system and emission sources in an SPA plant. The description of the scrubber system is almost identical to that on a WPPA plant and will not be repeated here.

The alternative controls for SPA process emissions are water-actuated Venturi scrubbers and Venturi scrubbers with optional packed section. Since the water-actuated Venturi is cocurrent and limited to one theoretical stage, it may be necessary to add a packed section for additional gas absorption. An absorption efficiency of 83% equivalent to 5 transfer units may be required to meet the standards of performance. The energy requirements for the two types of scrubbers are approximately equivalent. Water flow rate for the water-induced Venturi is 100 gallons per 1,000 SCFM while for the conventional Venturi, 20 gallons per 1,000 SCFM is required. The conventional Venturi, however, must overcome 10 inches of water pressure drop in the fan (19).

IGCI scrubber specifications for 300 T/day SPA plants to operate with gypsum pond water are shown in Table 5-7. The material of construction was limited to PVC, rubber-lined steel and FRP. Responding to these specifications several vendors submitted capital and annual control costs. Table 5-8 shows average costs on both water-actuated and conventional Venturi scrubbers. To update the capital costs to 1978 one should use an average correction factor of 1.79 which would give a total capital cost for 1335, 2620, 1335 and 2620 ACFM of \$16,500, \$21,100, \$42,900 and \$51,200, respectively.

Two existing submerged combustion plants would have to be retrofitted with SCFS to meet emission guidelines. Table 5-9 shows the cost of retrofitting (300 T/day P_2O_5) an SPA plant. The retrofit cost is based on replacement of the impingement scrubber with SCFS.

TABLE 5-6. RETROFIT COSTS FOR MODEL WPPA PLANT, CASE B (500 TONS/DAY P_2O_5) NOVEMBER 1974 (16) (25,000 SCFM SCRUBBER)

		Cost ($)
A.	Direct Items (installed)	
	1. Spray-cross flow packed bed scrubber	78,800
	2. Ductwork	20,000
	3. Piping	3,300
	4. Pump and motor	5,300
	5. Centrifugal fans and motors	16,000
	6. Removal of old equipment	12,500
	7. Stack	15,800
	8. Performance test	4,000
	Total Direct Items	155,700
B.	Indirect Items	
	Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A)	77,900
C.	Contingency (25% of A)	38,900
D.	Total Capital Investment	272,500
E.	Annualized Costs	
	1. Capital charges	44,400
	2. Maintenance	7,500
	3. Operating labor	2,000
	4. Utilities	9,300
	5. Taxes, insurance, administrative	10,900
	Total Annualized Costs	74,100

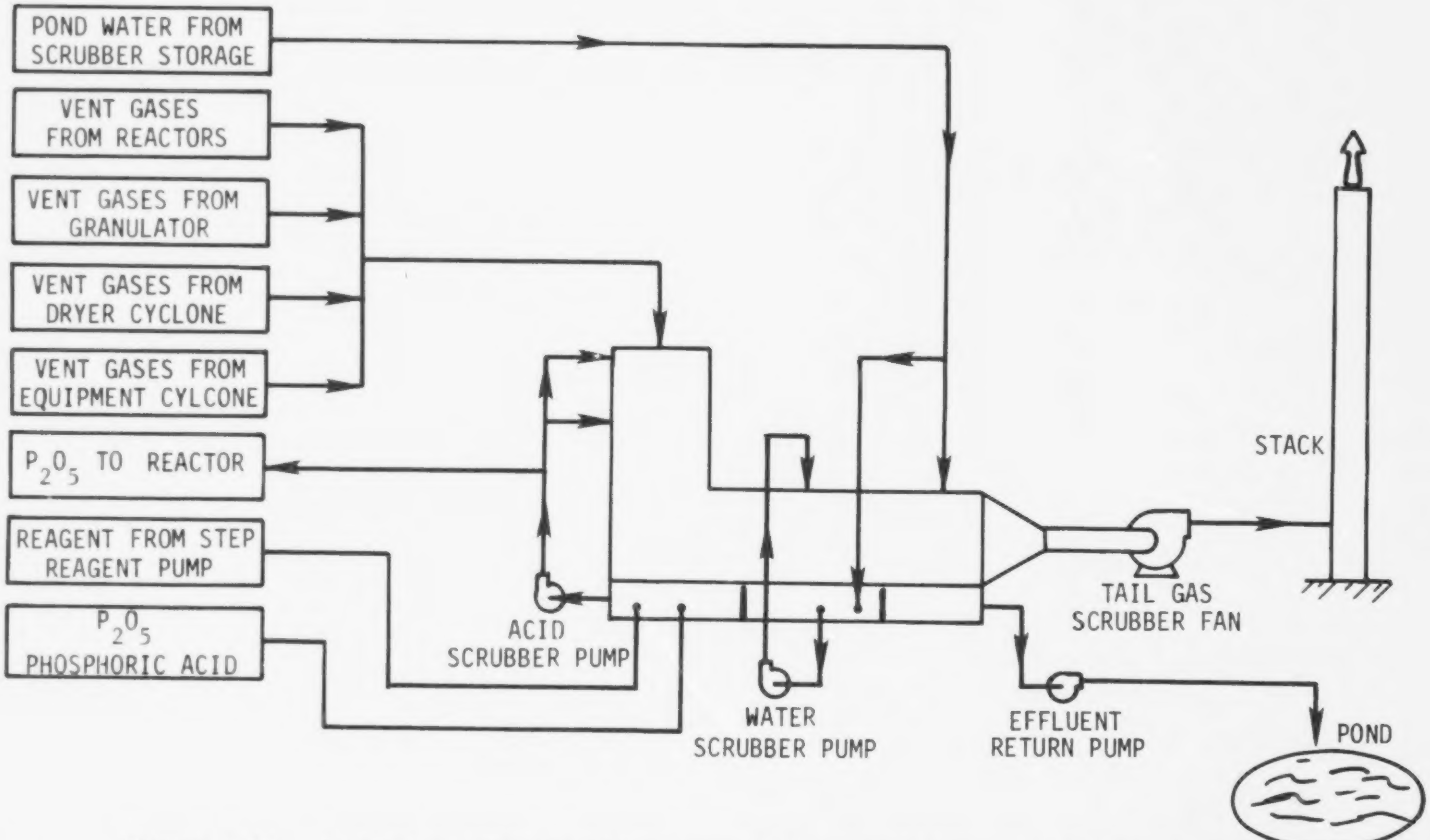

POND WATER FROM SCRUBBER STORAGE
VENT GASES FROM REACTORS
VENT GASES FROM GRANULATOR
VENT GASES FROM DRYER CYCLONE
VENT GASES FROM EQUIPMENT CYLCONE
P_2O_5 TO REACTOR
REAGENT FROM STEP REAGENT PUMP
P_2O_5 PHOSPHORIC ACID
ACID SCRUBBER PUMP
WATER SCRUBBER PUMP
EFFLUENT RETURN PUMP
TAIL GAS SCRUBBER FAN
STACK
POND

Figure 5-11: Spray-Crossflow Scrubber System in Superphosphoric Acid Plant

TABLE 5-7. OPERATING CONDITIONS FOR WET SCRUBBERS FOR SPA PROCESS COMBINED VENTS SPECIFICATION (20)

Plant Capacity, ton/day			300	
Acid Strength, Wt.% P_2O_5				
to Evaporator			54	
from Evaporator			72	
Fluorine Content, Wt.% F				
to Evaporator			1.5	
from Evaporator			0.4	
SCRUBBER Inlet Streams Source	Barometric Condenser	Hotwell	Cooling Chamber	Total To Scrubber
Flow, ACFM	287	2,120	264	2,671
Temp, °F	147.5	100	100	105
Flow, SCFM	250	2,000	250	2,500
Moisture, Vol%	24	6.7	6.7	7.8
Flow, DSCFM	190	1,880	234	2,304
Fluorine, ppm	10	5	30	8.25
Fluorine, lb/hr	0.008	0.030	0.024	0.062
Scrubber Outlet				
Flow, DSCFM				2,304
Temp, °F				100
Moisture, Vol%				6.7
Flow, SCFM				2,470
Fluorine, ppm				1,455
Fluorine, lb/hr				0.011
Scrubber Efficiency, %				82.5
Estimated y', ppm				1.4
Estimated NTU requirement				5.0

TABLE 5-8. CAPITAL AND ANNUAL CONTROL COSTS FOR SPA PLANTS VACUUM EVAPORATION (13) (1974 COSTS)

	Water Induced Venturi		Conventional Venturi	
Gas Flow Rate (ACFM) at 105°F	1,335	2,620	1,335	2,620
Capital Costs ($)				
Collector	6,400	8,600	6,300	7,700
Auxiliary equipment (fan, pumps, ductwork, instrumentation)	300	600	4,200	4,700
Installation Cost	2,500	2,600	13,600	16,200
TOTAL CAPITAL COST	9,200	11,800	24,100	28,600
Annual Cost ($/yr)				
Operating Labor	200	200	1,230	1,230
Maintenance	520	620	1,310	1,340
Utilities	880	1,430	990	1,770
Depreciation (10 yr)	920	1,180	2,410	2,860
Interest (8%)	740	940	1,930	2,290
Property Tax, Ins. (2%)	180	240	480	570
Administration (5%)	460	590	1,200	1,430
TOTAL ANNUAL COST	3,900	5,200	9,600	11,500

TABLE 5-9. RETROFIT COSTS FOR MODEL SPA PLANT (300 TONS/DAY P_2O_5)
NOVEMBER 1974 (16)

	Cost ($)
A. Direct Items (installed)	
1. Spray-crossflow packed bed scrubber	37,500
2. Ductwork	5,000
3. Piping	1,900
4. Pump and motor	4,200
5. Removal of old equipment	12,500
6. Performance test	4,000
Total Direct Items	64,300
B. Indirect Items	
Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A)	32,600
C. Contingency (25% of A)	16,300
D. Total Capital Investment	114,000
E. Annualized Costs	
1. Capital charges	18,600
2. Maintenance	3,000
3. Operating labor	2,000
4. Utilities	700
5. Taxes, insurance, administrative	4,400
Total Annualized Costs	28,700

5.5 Diammonium Phosphate (DAP)

The present emission guideline, which is equal to NSPS, limits fluoride emission from a DAP plant to 0.03 grams of fluoride (as F^-) per kilogram of P_2O_5. This guideline requires 85% fluoride removal which could be achieved by SCFS added to existing Venturis. Acceptable alternative scrubber combinations for a DAP plant are shown in Figure 5-12 (20). The two-stage scrubber combinations may be termed primary for particulate control and secondary for gaseous fluoride and ammonia removal.

The sources of emission and a primary-secondary scrubber combination for a well-controlled DAP plant are shown in Figure 5-13. The scrubbers in DAP plants are designed for ammonia recovery, particulate collection, and fluoride removal. The emission control in a DAP plant will be described in detail for three reasons:

1. DAP is a major phosphate fertilizer product and its importance is still increasing.
2. The control system is relatively complex.
3. Control equipment has been plagued with plugging and poor efficiency problems.

The ammonia recovery in Figure 5-13 is achieved in a coaxial scrubber described in Section 5.2.4. A major problem encountered in ammonia scrubbing by phosphoric acid is the stripping of fluoride. The degree of stripping depends on the temperature, acid and sulfate concentration, and the temperature in the scrubber is increased because of exothermic neutralization. The second problem resulting from ammonia absorption is formation of submicron aerosols of ammonium fluoride and ammonium bifluoride (17). These emissions are difficult to collect and the most economical solution appears to be the use of nucleators. The nucleator design is similar to that of a spray-crossflow scrubber but it uses four mechanisms of particulate collection when conducted with hydrophilic materials:

1. Condensation of water on the particulates at or above the dew point.
2. Agglomeration of the particulates by inelastic Brownian interception.
3. Short path inertial impact on small targets.
4. Thermophoretic collection in short paths to small target surfaces.

A critical factor in the efficiency of the nucleation process is the provision for short path inertial and thermophoretic capture. Commercial operating conditions allow submicron ammonium fluoride removal at a pressure drop of 2 inches of water (17). It is important to note that a conventional Venturi would require 20 to 50 inches of water to achieve the same goal. The SCFS is designed for high mass transfer efficiency with variable liquid flux so that the liquid can be concentrated in the zone of maximum collection. For example, maximum deposition in the packed bed will occur in the first foot of packing. Thus, the liquid irrigation rate can be

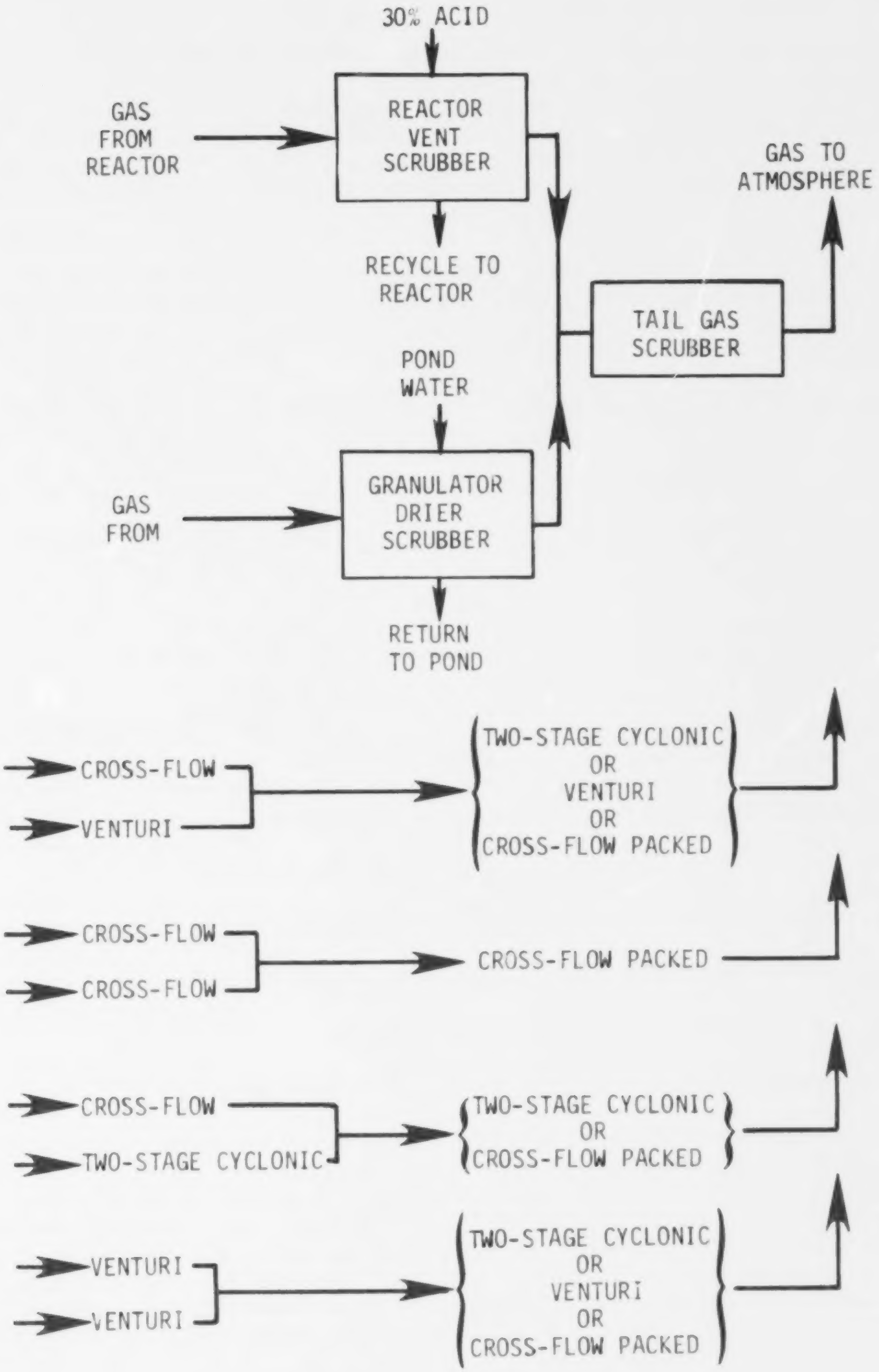
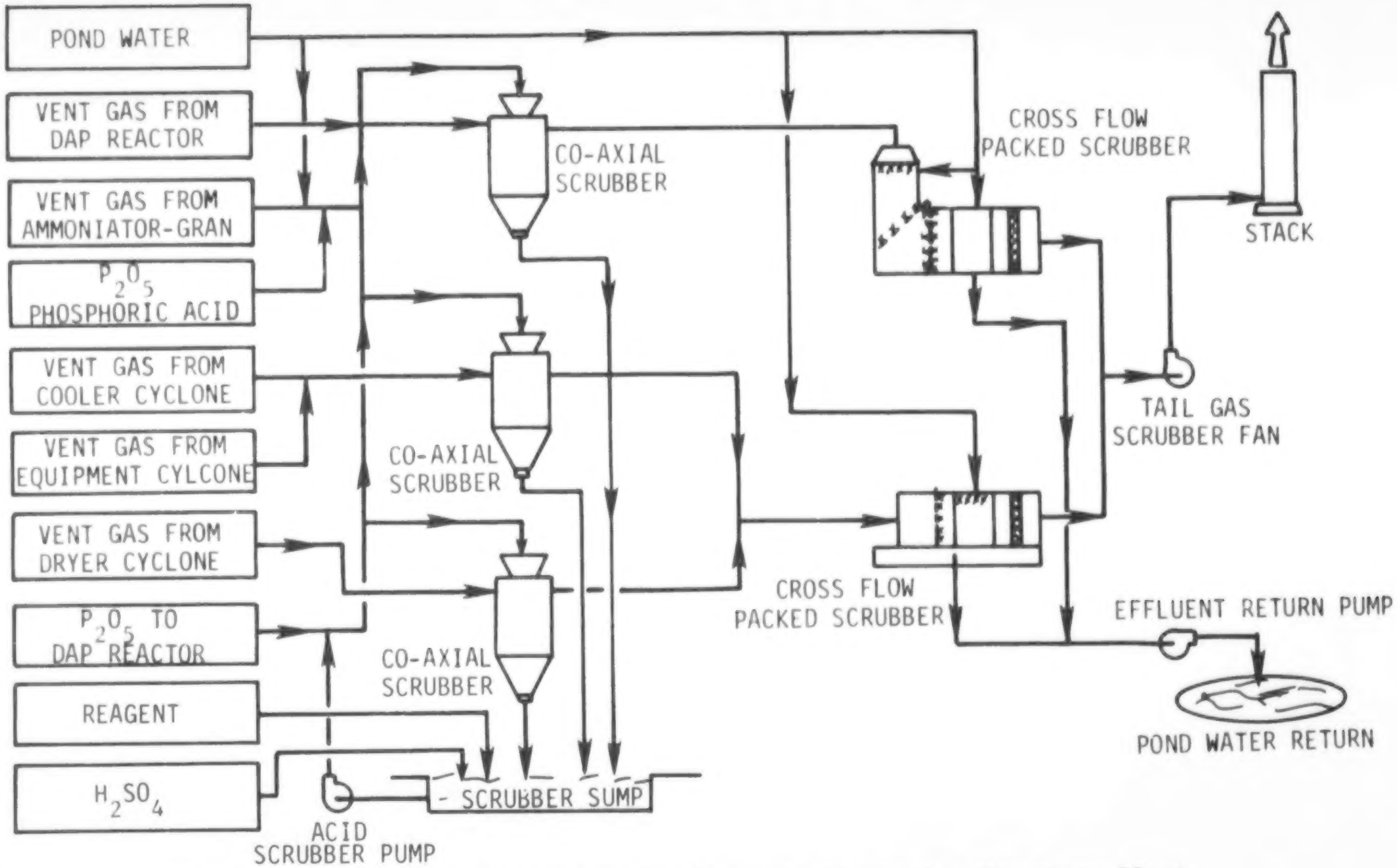

30% ACID
GAS FROM REACTOR
REACTOR VENT SCRUBBER
GAS TO ATMOSPHERE
RECYCLE TO REACTOR
TAIL GAS SCRUBBER
POND WATER
GAS FROM
GRANULATOR DRIER SCRUBBER
RETURN TO POND
CROSS-FLOW
VENTURI
TWO-STAGE CYCLONIC OR VENTURI OR CROSS-FLOW PACKED
CROSS-FLOW
CROSS-FLOW
CROSS-FLOW PACKED
CROSS-FLOW
TWO-STAGE CYCLONIC
TWO-STAGE CYCLONIC OR CROSS-FLOW PACKED
VENTURI
VENTURI
TWO-STAGE CYCLONIC OR VENTURI OR CROSS-FLOW PACKED

Figure 5-12: Acceptable Scrubber Combinations for DAP Process Plants (20)



POND WATER
VENT GAS FROM DAP REACTOR
VENT GAS FROM AMMONIATOR-GRAN
P_2O_5 PHOSPHORIC ACID
VENT GAS FROM COOLER CYCLONE
VENT GAS FROM EQUIPMENT CYLCONE
VENT GAS FROM DRYER CYCLONE
P_2O_5 TO DAP REACTOR
REAGENT
H_2SO_4
ACID SCRUBBER PUMP
SCRUBBER SUMP
CO-AXIAL SCRUBBER
CO-AXIAL SCRUBBER
CO-AXIAL SCRUBBER
CROSS FLOW PACKED SCRUBBER
CROSS FLOW PACKED SCRUBBER
STACK
TAIL GAS SCRUBBER FAN
EFFLUENT RETURN PUMP
POND WATER RETURN

Figure 5-13: Primary and Secondary Scrubbers in Diammonium PHosphate Plant

maintained at 20-30 GPM/ft^2 in the first foot of packing, whereas it can be as low as 5 GPM/ft^2 at the back portion of the packing (17).

Plugging of scrubbers in DAP plants used to be a serious problem until recently. In a scrubber system similar to one shown in Figure 5-3 such a problem was attributed to lack of sufficient attention and less than optimum system performance and control. A rigorous program of repairs, modifications, maintenance, and operation was instituted to solve the plugging problem. The primary modifications were (22):

1. Increase of clearance of axial downcomer to the coaxial cyclonic shell. Since this modification, there was no plugging in the primary scrubbers.

2. Separation of inlet headers on the primary scrubbers for cleanout ease.

3. Fresh water flush on the normal 8-10 days maintenance schedule to wash out any buildup on the primaries.

4. Increased open area of the grating of the nucleators.

5. Increased open area of the distributors in the nucleators.

Upon implementation of the above modifications and alert operation and maintenance, the plugging problem was resolved.

In many plants particulate carry-over was suspected or determined at the outlet of SCFS. Kimre mist eliminators were proven effective in alleviating this problem and a number of plants have retrofitted their scrubbers with them. The application of Kimre mist eliminators represent a recent development and a study to evaluate their efficiency will be outlined in a separate section (Section 9).

The IGCI prepared specifications for primary and secondary scrubbers in DAP plants, as shown in Tables 5-10 and 5-11 (20). Two stage wet cyclonic and Venturi scrubbers using pond water were specified as primary scrubbers, while crossflow packed scrubbers were specified as secondary scrubbers. Because of relatively high temperature PVC was ruled out as a material of construction, so rubber-lined steel or FRP was to be used. Table 5-12 shows the corresponding capital and annual control cost (19). Up-to-date costs can again be derived by using an average correction index of 1.79.

EPA tested SCFS in development of standards for the DAP process. Scrubber performance is shown in Table 5-13 (23).

The plant using the TVA process was considered for retrofit involving replacement of the cyclonic spray tower on the reactor-granulator stream with an SCFS and addition of SCFS as a tail gas unit to the dryer and cooler streams (16). Total capital and annualized cost estimates are shown in Table 5-14 (16).

TABLE 5-10. OPERATING CONDITIONS FOR PRIMARY SCRUBBERS FOR DAP PROCESS DRYER AND COOLER VENTS (20)

Plant Capacity, Ton/Day DAP	1,000	1,600
Plant Capacity, Ton/Day P_2O_5	500	800
Process Weight, Ton/Hr	42	66.7
Gas to Scrubber:		
Flow, DSCFM	30,000	48,000
Flow, SCFM	46,100	74,000
Flow, ACFM	55,700	89,000
Temp., °F	180	180
Moisture, vol. %	35	35
Particulate, gr/SCF	0.5	0.5
Particulate, Lb/Hr	200	320
Ammonia, Lb/Ton P_2O_5	8.0	8.0
Ammonia, Lb/Hr	167	267
Ammonia, ppm	1,350	1,350
Gas from Scrubber:		
Flow, DSCFM	30,000	48,000
Flow, SCFM	46,800	75,000
Flow, ACFM	53,500	85,500
Temp., °F	164	164
Mositure, vol. %	36	36
Particulate, gr/SCF	0.01	0.01
Particulate, Lb/Hr	4.0	6.4
Ammonia, Lb/Ton P_2O_5	0.08	0.08
Ammonia, Lb/Hr	1.67	2.67
Ammonia, ppm	13.4	13.4
Particulate Efficiency, wt. %	98	98
Ammonia Efficiency, %	99	99

TABLE 5-11. OPERATING CONDITIONS FOR SECONDARY SCRUBBERS FOR DAP PROCESS DRYER AND COOLER VENTS (20)

Plant Capacity, Ton/Day DAP	1,000	1,600
Plant Capacity, Ton/Day P_2O_5	500	800
Process Weight, Ton/Hr	42	66.7
Gas to Scrubber:		
Flow, DSCFM	30,000	48,000
Flow, SCFM	46,800	75,000
Flow, ACFM	53,500	85,500
Temp., °F	164	164
Moisture, vol. %	36	36
Fluorine, ppm as F-	15	15
Fluorine, Lb/Hr	2.1	3.35
Gas from Scrubber:		
Flow, DSCFM	30,000	48,000
Flow, SCFM	31,900	51,000
Flow, ACFM	33,700	54,000
Temp., °F	100	100
Mositure, vol. %	7	7
Medium Efficiency Case		
Fluorine, ppm as F-	4.1	4.1
Fluorine, Lb/Hr	0.415	0.67
Fluorine removal, %	80	80
Estimated y', ppm	1.95	1.95
Estimated NTU	1.80	1.80
High Efficiency Case		
Fluoride, ppm as F-	3.25	3.25
Fluoride, Lb/Hr	0.31	0
Fluorine removal, %	85	85
Estimated y'	1.95	1.95
Estimated NTU	2.8	2.8

TABLE 5-12. CAPITAL AND ANNUAL CONTROL COSTS FOR DIAMMONIUM PHOSPHATE PLANTS (19)

Model Plant Size (P_2O_5)	500 TPD		800 TPD	
Process Source	Primary Collector	Secondary Collector	Primary Collector	Secondary Collector
A. Reactor-Granulator				
1. Capital ($)	155,000(1)	60,000	210,000	83,400
2. Total Annual Cost ($)	62,500	23,000	87,400	32,100
B. Drier				
1. Capital ($)	162,000(2)	80,000	225,000	111,000
2. Total Annual Cost ($)	82,000	30,800	120,000	43,000
C. Cooler & Transfer Points				
1. Capital ($)	118,000(2)	57,000	164,000	79,200
2. Total Annual Cost ($)	47,000	22,100	83,000	30,800
Summary				
Total Capital ($)	632,000		873,000	
Total Annual Cost ($)	277,400		396,300	
Unit Control Cost ($/ton P_2O_5)	1.68(3)		1.50	
Unit Control Cost with NH_3 credits(4) ($)	0.88		0.70	

---

(1) Two-Stage cyclonic for both model plant sizes.

(2) Venturi cyclone for both model plant sizes.

(3) 330 days per year operation.

(4) Value of NH_3 taken at $40 per ton. Recovered NH_3 is estimated at 80 lbs per ton NH_3 feed for all sources combined.

TABLE 5-13. SPRAY-CROSSFLOW PACKED BED SCRUBBER PERFORMANCE IN DIAMMONIUM PHOSPHATE AND GRANULAR TRIPLE SUPERPHOSPHATE PLANTS (23)

Type Of Facility	Sources Controlled	Primary Controls	Secondary Controls	Fluoride Emissions[a] (lb F/ton P_2O_5)
DAP	reactor, granulator drier, and cooler	3 venturi scrubbers in parallel[b]	3 spray-crossflow packed bed scrubbers in parallel	0.034, 0.029[c]
DAP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel[b]	3 spray-crossflow packed bed scrubbers in parallel	0.039
GTSP	reactor, granulator, drier, and cooler	3 venturi scrubbers in parallel	3 spray-crossflow packed bed scrubbers in parallel	0.18, 0.06[c]
GTSP	reactor, granulator, drier, and cooler	process gases combined and sent to 2 venturi scrubbers in parallel followed by a cyclonic scrubber	spray-crossflow packed bed scrubber	0.21
GTSP storage	storage building	--	spray-crossflow packed bed scrubber	0.00036[d]

[a] Average of testing results.

[b] Weak phosphoric acid scrubbing solution.

[c] Second series of tests.

[d] Emission rate is in terms of pounds F per hour per ton of P_2O_5 in storage.

TABLE 5-14. RETROFIT COSTS FOR MODEL DAP PLANT (500 tons/day P_2O_5) November 1974 (16)

			Costs ($)
A.	Direct Items (installed)		
	1.	Spray-crossflow packed bed scrubbers (3)	$ 285,000
	2.	Ductwork	16,700
	3.	Piping	26,200
	4.	Pumps and motors	41,500
	5.	Centrifugal fans and motors	33,000
	6.	Removal of old equipment	12,500
	7.	Performance test	4,000
	Total Direct Items		418,900
B.	Indirect Items		
	Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A)		209,500
C.	Contingency (25% of A)		104,700
D.	Total Capital Investment		733,100
E.	Annualized Costs		
	1.	Capital charges	119,500
	2.	Maintenance	20,000
	3.	Operating labor	4,000
	4.	Utilities	21,200
	5.	Taxes, insurance, administrative	29,400
	Total Annualized Costs		194,100

5.6 Normal Superphosphate (NSP)

Sources of emissions at an NSP plant include the mixer, den, and curing building. Emissions of fluoride and particulate from the mixer and den are controlled by a scrubbing system using recycled water. Figure 5-14 shows a scrubbing system on an ROP-NSP plant. The emissions from the mixer are controlled in a two stage centrifugal spray scrubber while the emissions from the den undergo one stage scrubbing.

Since the process for production of ROP-NSP and emission control is almost identical to that for an ROP-TSP facility, the control technology evaluation presented in the next section applies to ROP-NSP.

5.7 Triple Superphosphate (TSP)

The present emission guideline for fluoride emission from GTSP and ROP-TSP (including storage) calls for 0.1 gram fluoride (as F^-) per kilogram of P_2O_5 which is equal to the NSPS. This requires reduction of 99.6% of fluoride from the production facility which can be achieved in a two stage system. Figure 5-15 shows a typical scrubbing system at an ROP-TSP plant. This plant displays an efficient control system since most emissions undergo three stage scrubbing. The third stage is a spray chamber called a tail scrubber where combined emissions from upstream scrubbed sources are treated prior to discharge through the stack. The first stage is a Venturi scrubber primarily used for particulate removal followed by a cyclonic scrubber for fluoride scrubbing. Best Control Technology calls for SCFS as an alternative for a second stage because it has higher absorption efficiency than the cyclonic scrubber. Table 5-13 shows SCFS performance in a GTSP plant.

IGCI scrubber specifications for 250 and 400 T/day GTSP plants are shown in Table 5-15. The material of construction was limited to PVC, rubber-lined steel and FRP while pond water was to be used as a scrubbing liquid.

Table 5-16 shows the capital and annual costs obtained from the equipment vendors. The scrubber capital costs, translated to 1978 figures, add up to $1,500,000 for 250 T/day and 2,080,000 for 400 T/day. Table 5-17 shows engineering specifications, capital and annual costs for ROP-TSP scrubbers. In 1978 dollars, capital scrubber (installed) costs would be $412,000 for a 250 T/day plant and $589,000 for a 400 T/day plant.

In order to meet 99.6% fluoride emission efficiency, a typical retrofit would involve the replacement of the spray tower with SCFS. About 40% of ROP-TSP plants are directly affected by the emission guideline. The costs for retrofit are more severe than for other sources (because of large gas volumes) but are expected to be manageable. Table 5-18 shows the cost of replacing a spray tower with SCFS in a conventional TVA process plant (ROP-TSP). The Dorr-Oliver process is normally used for the production of GTSP. Existing control technology usually consists of a Venturi scrubber and cyclonic spray tower. The cost of replacing a spray tower with SCFS involving major retrofit is shown in Table 5-19.

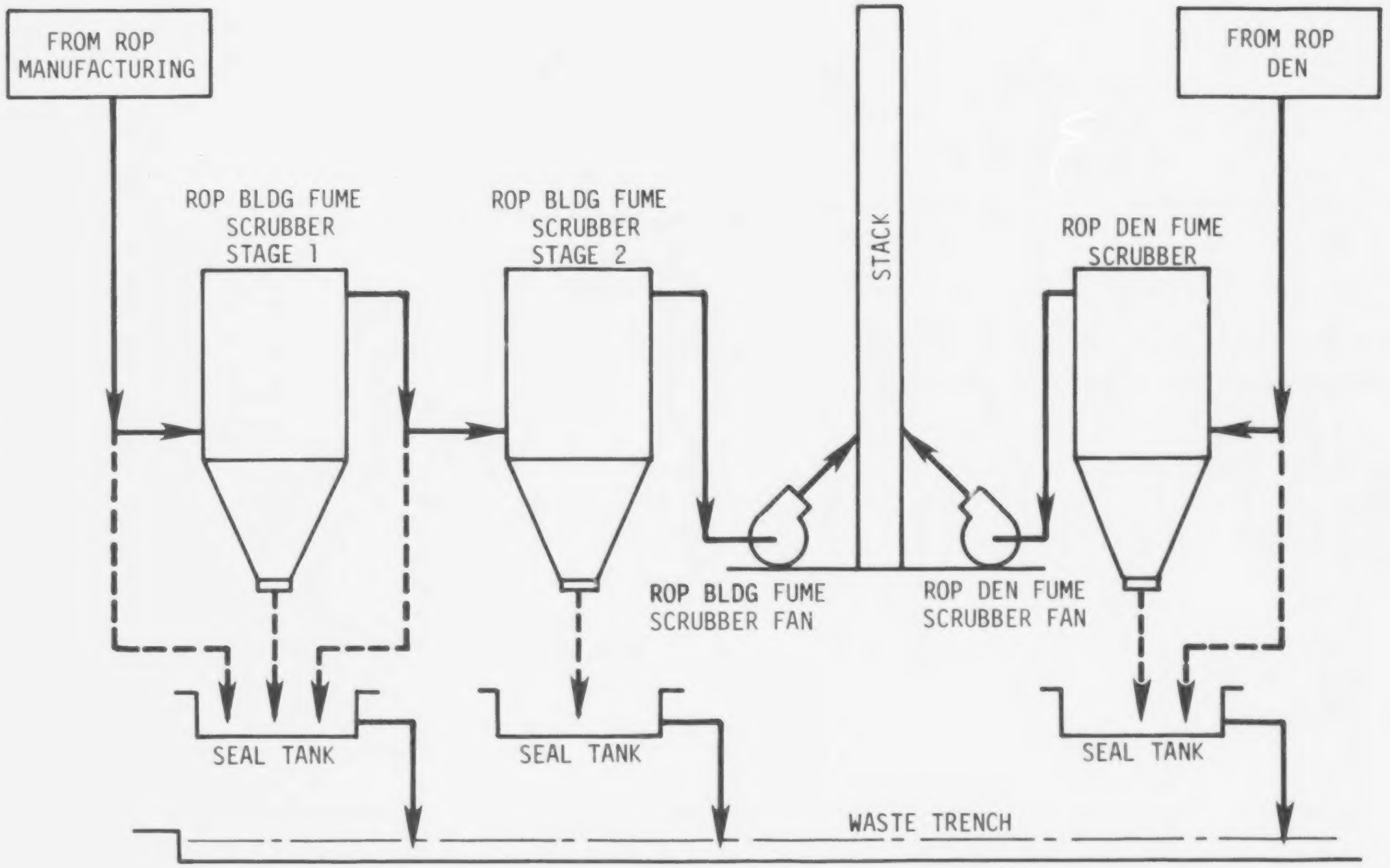

FROM ROP MANUFACTURING
ROP BLDG FUME SCRUBBER STAGE 1
ROP BLDG FUME SCRUBBER STAGE 2
STACK
FROM ROP DEN
ROP DEN FUME SCRUBBER
ROP BLDG FUME SCRUBBER FAN
ROP DEN FUME SCRUBBER FAN
SEAL TANK
SEAL TANK
SEAL TANK
WASTE TRENCH

Figure 5-14: Scrubbing System on Run-of-Pile Normal Superphosphate Plant

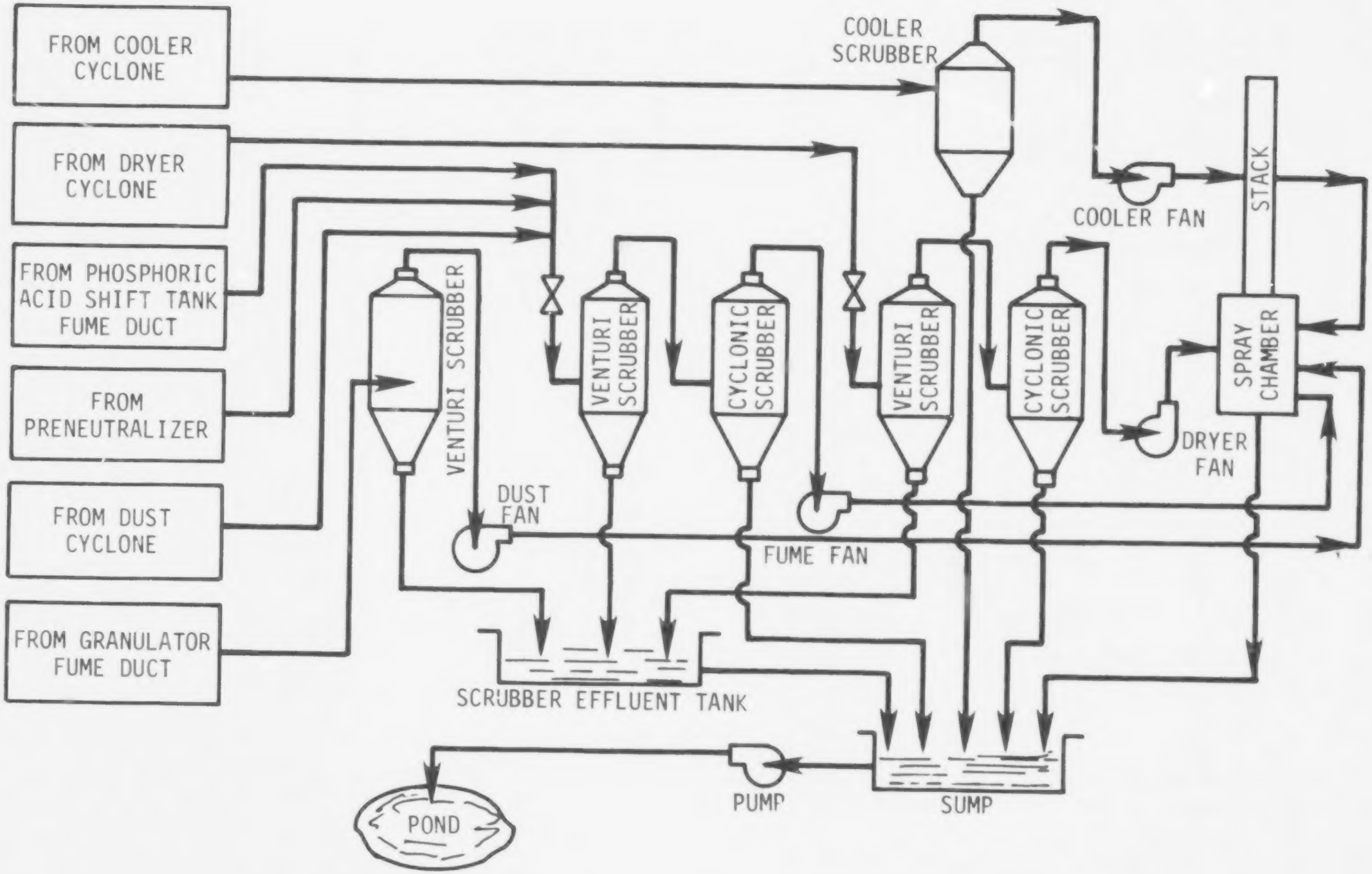

FROM COOLER CYCLONE
FROM DRYER CYCLONE
FROM PHOSPHORIC ACID SHIFT TANK FUME DUCT
FROM PRENEUTRALIZER
FROM DUST CYCLONE
FROM GRANULATOR FUME DUCT
VENTURI SCRUBBER
VENTURI SCRUBBER
CYCLONIC SCRUBBER
VENTURI SCRUBBER
CYCLONIC SCRUBBER
COOLER SCRUBBER
COOLER FAN
STACK
SPRAY CHAMBER
DRYER FAN
DUST FAN
FUME FAN
SCRUBBER EFFLUENT TANK
SUMP
PUMP
POND

Figure 5-15: Scrubbing System on Run-of-Pile Triple Superphosphate Plant

TABLE 5-15. ENGINEERING SPECIFICATIONS FOR ESTIMATING COSTS FOR GRANULAR TRIPLE SUPERPHOSPHATE PLANTS (19)

Model Plant Size (P_2O_5)	250 TPD		400 TPD	
	Primary Collector	Secondary Collector	Primary Collector	Secondary Collector
A. Reactor- Granulator				
Effluent Volume, DSCFM	20,000	20,000	32,000	32,000
Gas to Scrubber, ACFM	25,400	22,700	40,600	36,300
Moisture Content, %	11	7	11	7
Gas Temperature, °F	140	100	140	100
B. Drier				
Effluent Volume, DSCFM	40,000		64,000	
Gas to Scrubber, ACFM	54,700		87,000	
Moisture Content, %	12		12	
Gas Temperature, °F	180		180	
C. Cooler-Transfer Points				
Effluent Volume, DSCFM	50,000		80,000	
Gas to Scrubber, ACFM	58,000		93,000	
Moisture Content, %	3		3	
Gas Temperature, °F	140		140	
D. Storage				
Effluent Volume, DSCFM	98,400		157,400	
Gas to Scrubber, ACFM	100,000		160,000	
Moisture Content, %	2		2	
Gas Temperature, °F	80		80	

TABLE 5-16. CAPITAL AND ANNUAL CONTROL COSTS FOR GRANULAR TRIPLE SUPERPHOSPHATE PLANTS (19) (1974 COSTS)

Model Plant Size (P_2O_5)	250 TPD		400 TPD	
	Primary Collector	Secondary Collector	Primary Collector	Secondary Collector
A. Reactor-Granulator				
1. Capital	93,300[1]	43,700	130,000	60,700
2. Total Annual Costs	44,300	17,000	64,000	23,400
B. Drier				
1. Capital	179,000[2]		247,000	
2. Total Annual Costs	106,500		157,000	
C. Cooler & Transfer Points				
1. Capital	186,000[2]		259,000	
2. Total Annual Costs	111,700		160,000	
D. Storage				
1. Capital	335,000[3]		465,000	
2. Total Annual Costs	140,000		202,000	

Summary	250 TPD	400 TPD
Total Capital ($)	837,000	1,162,000
Total Annual Cost ($/yr)	420,000	606,000
Unit Control Cost ($/ton P_2O_5)	5.09	3.67

[1] Venturi-cyclone on both model plant sizes.
[2] Venturi-packed type on both model plant sizes.
[3] Cyclonic scrubber on both models.

NOTE: Pond water scrubbing media for all control devices.

TABLE 5-17. CAPITAL AND ANNUAL CONTROL COSTS FOR RUN-OF-PILE TRIPLE SUPERPHOSPHATE PRODUCTION (19) (1974 COSTS)

Model Plant Size (P_2O_5)	250 TPD	400 TPD
A. Engineering Specifications:		
Gas to Scrubber, ACFM	60,000	100,000
Collector	Venturi Cyclone	Venturi Cyclone
Scrubbing Media	Pond Water	Pond Water
B. Cost Summary		
1. Capital Requirements ($)	230,000(1)	329,000(2)
2. Total Annual Cost ($)	102,000	153,000
3. Unit Control Costs ($ per ton P_2O_5)	1.24	1.16

(1) Scrubber portion of costs if $44,000, auxiliary and installation costs are $186,000.

(2) Scrubber portion of costs is $66,000; auxiliary and installation costs are $263,000.

TABLE 5-18. RETROFIT COSTS FOR MODEL ROP-TSP PLANT, CASE A (550 tons/day P_2O_5) November 1974 (16)

		Costs ($)
A.	Direct Items (installed)	
	1. Spray-crossflow packed bed scrubbers	$ 294,000
	2. Ductwork	9,800
	3. Piping	33,300
	4. Pumps and motors	31,900
	5. Centrifugal fans and motors	28,800
	6. Removal of old equipment	12,500
	7. Stack	44,000
	8. Performance test	4,000
	Total Direct Items	458,300
B.	Indirect Items	
	Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A)	229,200
C.	Contingency (25% of A)	114,600
D.	Total Capital Investment	802,100
E.	Annualized Costs	
	1. Capital charges	130,700
	2. Maintenance	21,700
	3. Operating labor	4,000
	4. Utilities	26,500
	5. Taxes, insurance, administrative	32,000
	Total Annualized Costs	214,900

TABLE 5-19. RETROFIT COSTS FOR MODEL GTSP PLANT (400 tons/day P_2O_5) November 1974 (16)

				Costs
A.	Direct Items (installed)			
	1.	GTSP Production		
		a.	Spray-crossflow packed bed scrubbers (3)	$ 261,000
		b.	Ductwork	22,800
		c.	Piping	26,200
		d.	Pumps and motors	35,900
		e.	Removal of old equipment	18,000
		f.	Performance test	4,000
		g.	Centrifugal fans and motors	14,400
	2.	GTSP Storage		
		a.	Crossflow packed scrubber	150,000
		b.	Ductwork	56,600
		c.	Piping	27,800
		d.	Pumps and motors	19,400
		e.	Centrifugal fan and motor	23,000
		f.	Structural steel supports/building	50,000
		g.	Sealing of storage building	10,000
		h.	Performance test	4,000
	Total Direct Items			723,100
B.	Indirect Items			
	Engineering construction expense, fee, interest on loans during construction, sales tax, freight insurance (50% of A)			361,600
C.	Contingency (25% of A)			180,800
D.	Total Capital Investment			1,265,500
E.	Annualized Costs			
	1.	Capital charges		206,300
	2.	Maintenance		33,800
	3.	Operating labor		6,000
	4.	Utilities		40,600
	5.	Taxes, insurance, administrative		50,500
	Total Annualized Costs			337,200

Uncontrolled emissions from ROP-TSP and GTSP storage emissions present major fluoride emissions from stationary sources in the phosphate fertilizer industry. Adoption of the emission guidelines would result in a 50% emission reduction for GTSP and 90% for ROP-TSP (16). The present emission guideline for a GTSP storage facility limits fluoride emissions to 2.5×10^{-4} grams per hour per kilogram of P_2O_5 in storage.

These limitations can be easily reached by applying SCFS on the storage facility. Recycled gypsum pond water can be used as a scrubbing liquid.

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6.0 GYPSUM POND EMISSIONS AND CONTROLS

6.1 Location, Description and Role of the Gypsum Pond

The gypsum pond is an integral part of the wastewater treatment scheme at a phosphate fertilizer plant and it serves two functions as both a settling and storage area for waste by-product gypsum and fluorine compounds, and as an area for atmospheric evaporative cooling of the pond water prior to its return to process units. The pond system operates in a closed loop mode and releases water for treatment only during heavy rainfall. The size of the pond at a WPPA plant is approximately 2.23×10^{-3} Km^2/metric ton P_2O_5/day (1). The surface area ranges from 0.26 to 2.71 Km^2.

The majority of gypsum ponds in the United States are located in the Polk-Hillsborough County area of Florida. Figure 6-1 shows the location of several gypsum ponds in that area.

There are three major considerations of environmental significance regarding gypsum ponds (2):

1. Civil engineering design to ensure mechanical integrity.
2. Process engineering consideration of water management and recycle uses.
3. Chemical processes that control fluorine behavior.

The chemistry of fluorine behavior is fundamental to virtually all aspects of environmental control and will be discussed next. Figure 6-2 shows the interrelationship of the storage pond system to the total phosphate manufacturing process (2). Fluoride transport to the gypsum pond system follows two basic pathways: Fluorides delivered from the acidulation process as by-product wastes consigned to the gypsum storage section and fluoride recovered in recycled process water uses and returned to the pond water storage section where effluents are mixed.

General operating parameters which affect fluoride loading in the gypsum pond for all phosphoric acid and phosphate fertilizer unit processes are as follows (1):

a. Product specification
b. Raw material specification
c. Temperature of the reactions
d. Acid concentration
e. Fluoride emissions standards
f. Fluoride recovery (if any).

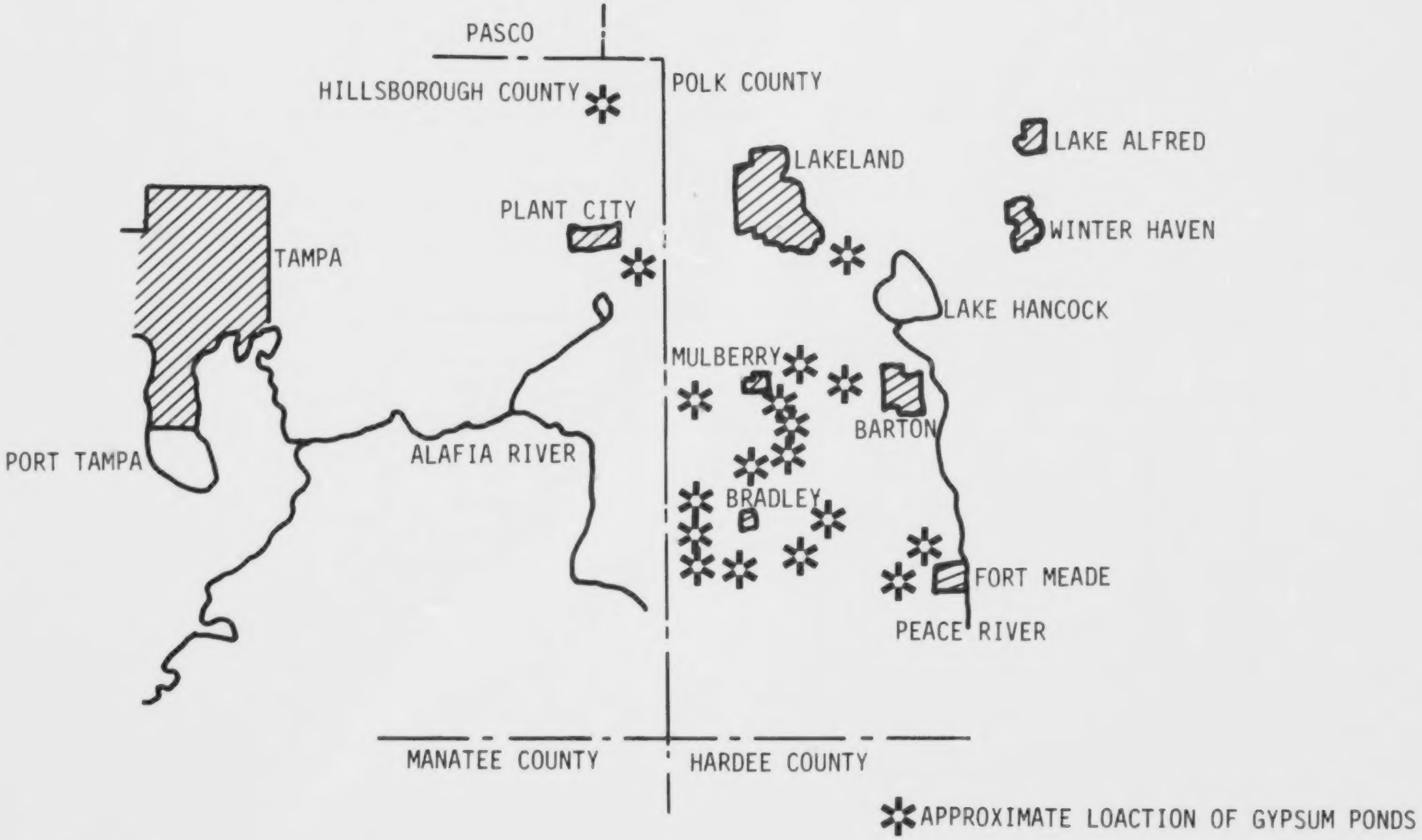
PASCO
HILLSBOROUGH COUNTY
POLK COUNTY
LAKE ALFRED
LAKELAND
PLANT CITY
WINTER HAVEN
TAMPA
LAKE HANCOCK
MULBERRY
BARTON
PORT TAMPA
ALAFIA RIVER
BRADLEY
FORT MEADE
PEACE RIVER
MANATEE COUNTY
HARDEE COUNTY
APPROXIMATE LOACTION OF GYPSUM PONDS

Figure 6-1: Approximate Locations of Gypsum Ponds in Central Florida

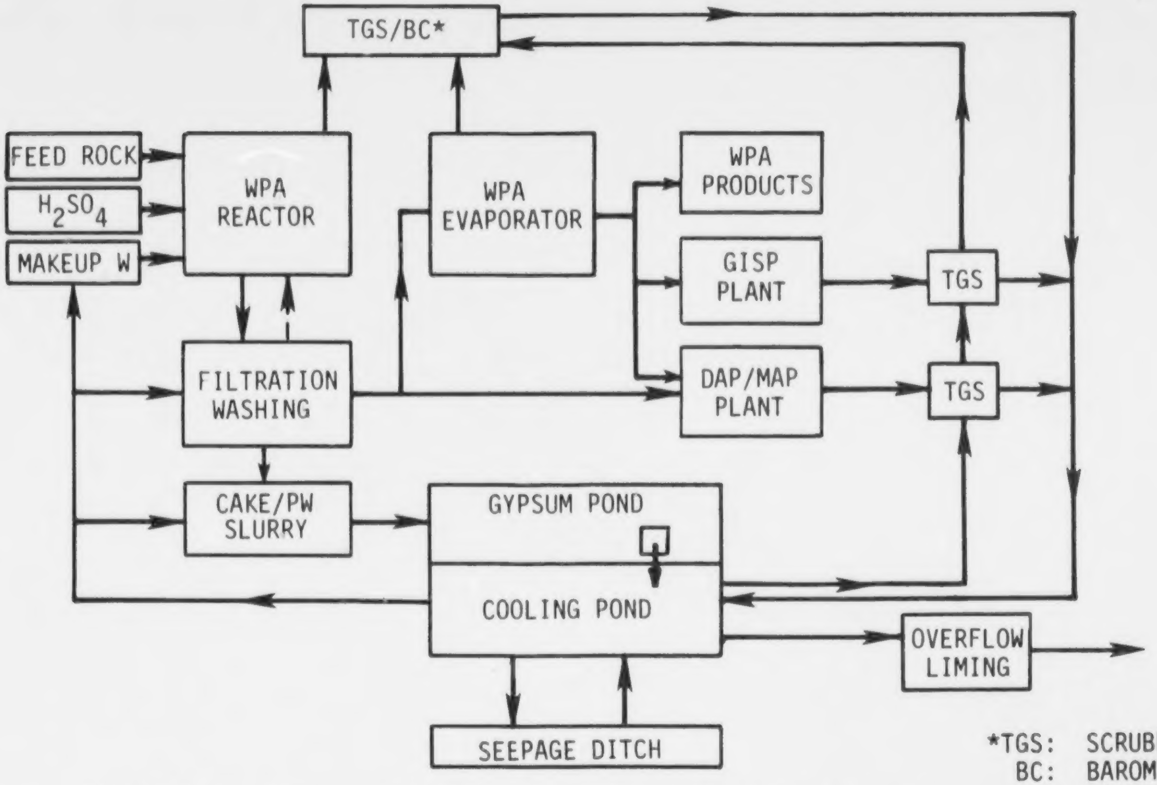
TGS/BC*
FEED ROCK
H_2SO_4
MAKEUP W
WPA REACTOR
WPA EVAPORATOR
WPA PRODUCTS
GISP PLANT
DAP/MAP PLANT
TGS
TGS
FILTRATION WASHING
CAKE/PW SLURRY
GYPSUM POND
COOLING POND
OVERFLOW LIMING
SEEPAGE DITCH

Figure 6-2: Fluorine Distribution: Interrelation of Gypsum Pond System to the Total Process (2)

*TGS: SCRUBBERS
BC: BAROMETRIC CONDENSER

A major operational parameter in phosphoric acid production is control of the crystalline form of calcium sulfate in the acidulation/filtration process.

6.2 Gypsum Pond Chemistry

One important role of the gypsum pond is to remove fluorides from the fertilizer manufacturing process. Table 6-1 indicates that over 50% of the soluble fluorides generated in the manufacture of phosphate fertilizers "disappears" in the pond (4). The major concern in studying gypsum pond chemistry will be establishing what fluoride species are likely to escape to the atmosphere and in what form fluoride is fixated in the pond.

Gypsum pond water is a complex mixture of various chemical species. Table 6-2 (3) shows some of the major cations and anions present. Fluorine, designated as F^- in Table 6-1, will occur as the fluoride ion F^-, as H_2SiF_6, HF (aq), SiF_4, HF_2^- and complexed with metals such as FeF_3, $AlFe^{++}$, AlF_2^+, AF_3, AF_4^-, etc.

Since one would like to immobilize as much fluorine as possible in the pond, the first important question is what modes of phosphate precipitation are possible. Table 6-3 shows the composition of 12 fluoride precipitates. A laboratory study was carried out to determine the impurity factors that favor the formation of chukhrovite ($Ca_4AlSiSO_4F_{13} \bullet 10\ H_20$) over the usual alkali fluorosilicates and possibly other major fluoride compositions such as ralstonite ($Na_xMg_xAl_{2-x}\ (F,0H)_6 \bullet H_20$) and cryolite ($Na_2SiF_6$). The major effects are due to aluminum and magnesium. High alumina concentrations favor chukhrovite, while a high magnesium content supresses fluoride precipitation. Increasing the sodium content favors the formation of Na_2SiF_6 as a competing precipitation process with chukhrovite. Laboratory test results indicate that the preferential precipitation of chukhrovite during the rock digestion stage can remove as much as 85% of the input fluorine. The fluorine can be immobilized in the by-product cake in a salt that will minimize fluorine redistribution in gypsum ponds. This is an effective way of controlling fluoride emissions but it is not fully understood. Because of decreasing phosphate rock purity, further study is recommended and will be described as a proposed research project in Section 9.

The transport of fluoride from pond water to the vapor phase is obviously one of the principal environmental concerns. The chemical equilibrium governing fluoride emissions involves the complicated interactions of HF, HF_2^-, H_2SiF_6, SiF_4, and SiO_2. These reactions are as follows:

$$H_2SiF_6(aq) \rightleftharpoons 2HF(aq) + SiF_4(aq)$$

$$3SiF_4(aq) + 2H_2O \rightleftharpoons 2H_2SiF_6(aq) + SiO_2(s)$$

$$SiO_2(s) + 6HF(aq) \rightleftharpoons H_2SiF_6(aq) + 2H_2O$$

$$HF(aq) + F^- \rightleftharpoons HF_2^-$$

TABLE 6-1. FLUORINE INVENTORY 700 TPD P_2O_5 PRODUCTION FLORIDA ROCK (4)

	LB/DAY
INPUT	
Fluoride in rock	170,000
OUTPUT	
Solid Fluorides	
In Gypsum	46,000
In Fertilizer Product	17,000
Total Solid Fluorides	63,000
Soluble Fluorides	
Lost to atmosphere from pond	50
Lost to atmosphere from stacks	40
Lost to pond discharge and seepage	14,000
"Disappeared"	92,910
Total Soluble Fluorides	107,000

TABLE 6-2. MAJOR CATION AND ANION CONCENTRATIONS IN GYPSUM POND WATER (3)

CATIONS	CONCENTRATION (mg/l)	CONCENTRATION (M)
Ca^{++}	2000	0.05
Na^{+}	1600	0.07
Al^{3+}	500	0.018
Fe^{3+}	300	0.005
Mg^{++}	240	0.01
K^{+}	200	0.005
H^{+}	pH = 1.4	0.04
ANIONS		
F^{-}	8000	0.42
SO =	4800	0.05
Cl-	200	0.006
$H_2PO_4^{-}$	1000	0.02

TABLE 6-3. POSSIBLE MODES OF F PRECIPITATION IN F.G. WAP SOLUTION (2)

FLUOSILICATES	FLUOALUMINATES
Na_2SiF_6	Na_3AlF_6
$NaKSiF_6$	Na_2KAlF_6
K_2SiF_6	$Ca_3(AlF_6)_2 \cdot 4H_2O$
$CaSiF_6 \cdot 2H_2O$	$(Mg_xNa_yAl_z)AlF_6 \cdot 2H_2O$
$MgSiF_6 \cdot 6H_2O$	

SIMPLE FLUORIDES	COMPLEX FLUORIDES
CaF_2	$Ca_4AlSiSO_4F_{13} \cdot 10H_2O$
MgF_2	

F DISTRIBUTED TO CAKE (% OF INPUT)	
Na_2SiF_6	20-30%
$(NaMg)_xAl_{2-x}F_6 \cdot 2H_2)$	_ 70%
$Ca_4AlSiSO_4F_{13} \cdot 10H_2O$	80-85%

$$3HF_2^- + SiO_2(s) + 3H^+ \rightleftharpoons H_2SiF_6(aq) + 2H_2O$$

$$HF(aq) \rightleftharpoons H^+ + F^-$$

$$HF(aq) \longleftarrow HF(v)$$

$$SiF_4(aq) \rightleftharpoons SiF_4(v)$$

The above reactions are overwhelmingly complex and can be considered only qualitatively. The first reaction equilibrium appears to be rate controlling but others (e.g., SiO_2) can play significant roles.

Figure 6-3 shows the reaction pathways considered to be the most significant in a gypsum pond. This simplified model meets the criteria that all chemical species entering the pond must either precipitate into the pond sediments or volatilize, and that waters in the pond are near saturation with respect to many chemical species due to continuous recycling.

The fluoride species involved and the quantities in which they are emitted to the atmosphere will be discussed next.

6.3 Gypsum Pond Air Emissions

Three studies have been conducted in an attempt to determine the amounts of fluoride emitted from gypsum ponds. The first study was performed in 1967 (5). It consisted of measuring fluoride concentrations emitted from a small A-frame structure placed on a 0.64 Km^2 gypsum pond. The intent of this study was to practically measure an emission rate. Unfortunately, due to the fundamental errors caused by using arbitrary areas and flow rate, the results are meaningless (1). A major study was conducted in 1970 (6). This study consisted of two phases. In the first phase, saturation vapor pressure of fluorides over a liquid solution of hydrofluoric acid (HF) and fluosilicic acid (H_2SiF_6) was measured. The results showed that a linear relationship exists between fluoride concentrations and fluoride vapor pressures above the solution. The second phase was concerned with the determination of a fluoride emission factor and involved experiments in a wind tunnel. Figure 6-4 shows the study's summary of results on process water.

What is probably the most complete study on fluoride emissions from gypsum ponds was conducted in 1974 (7). The approach to the development of an emission factor was:

1. Development of a correlation for predicting the mass transfer coefficient (K_f) from existing data.
2. Measurement of the equilibrium vapor pressure (P_f^*) of fluorides over samples of pond water.
3. Prediction of fluoride mass transfer rates by the equation:

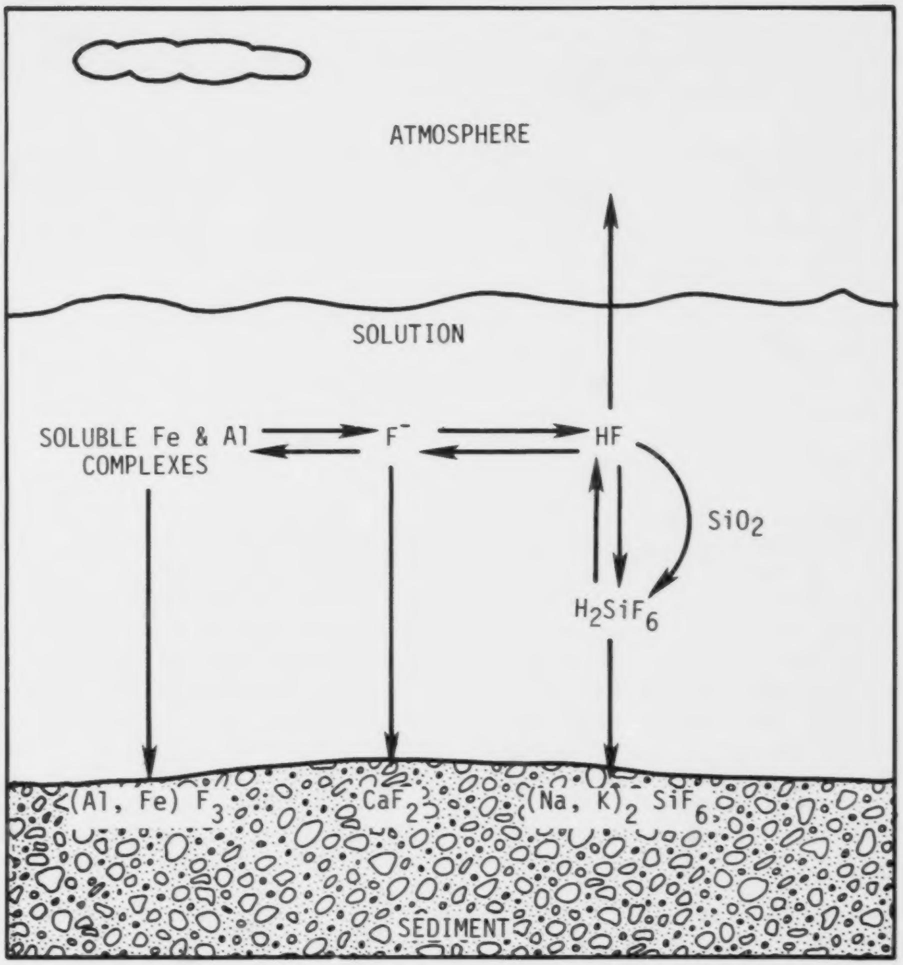
ATMOSPHERE
SOLUTION
SOLUBLE Fe & Al COMPLEXES
F^-
HF
SiO_2
H_2SiF_6
(Al, Fe) F_3
CaF_2
$(Na, K)_2\ SiF_6$
SEDIMENT

Figure 6-3: Major Gypsum Pond Equilibrium

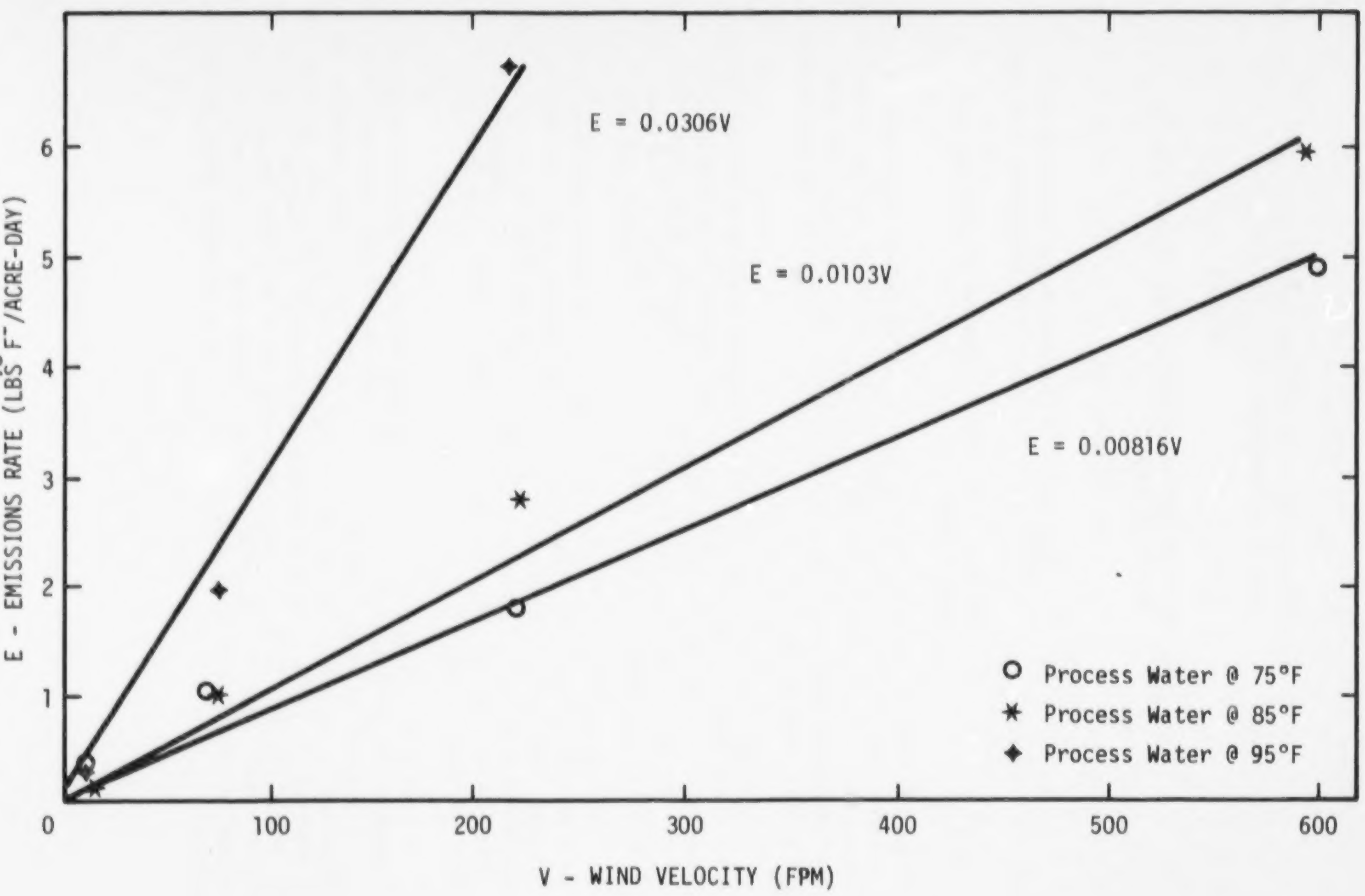

Figure 6-4: Emission Factors for Process Water at 75°, 85°, 95°F (6)

$$N_f = K_f (P_f^* - P_f)$$

where

N_f = Fluoride transfer rate per unit surface area from pond to atmosphere $\frac{(\text{g-moles f})}{(\text{hr-M}^2)}$

K_f = Overall gas-side fluoride mass transfer coefficient $\frac{(\text{g-moles F}\ \ )}{(\text{hr-M}^2\text{-mm Hg})}$

P_f^* = Partial pressure of fluoride at the gas liquid interface in equilibrium with pond water (mm Hg)

P_f = Partial pressure of fluorides in the atmosphere above pond.

Figure 6-5 shows fluoride emission factors developed as a function of temperature and wind speed. A simulation model for fluoride concentration prediction was also developed. The model was verified through field sampling and analysis, but the correlation between measured and calculated ambient air concentrations is somewhat questionable (1).

Comparisons of emission factors developed in these studies are shown in Table 6-4. These results should be interpreted with caution because a judgment cannot be made as to the validity of either method of estimation when applied to a particular pond. The best statement that can be made at this point is that the characteristic emission factor appears to lie in the range of 0.1 to 10lb/acre-day (1).

In August 1977, TRC - THE RESEARCH CORPORATION of New England and EPA jointly carried out a field program at the CF Industries-Bartow Phosphate Complex near Bartow, Florida. The purposes of the program were to evaluate the ROSE (Remote Optical Sensing of Emission) system for the measurement of fluoride concentrations above and at the edge of the gypsum pond and to estimate the fluoride emission rate.

During the program wet sampling/analysis was employed to determine the concentration of total fluoride concentrations upwind and downwind of the gypsum pond. Vertical fluoride concentrations up to 25 meters were obtained through the elevation of sampling probes with a crane. Together with the wet sampling (conducted by TRC), a remote sensing measurement (conducted by EPA) was performed using the ROSE system consisting of a long-path Fourier-transform IR spectrometer system. A meteorological monitoring station was erected in the middle of the gypsum pond area to collect meteorological data during the field program.

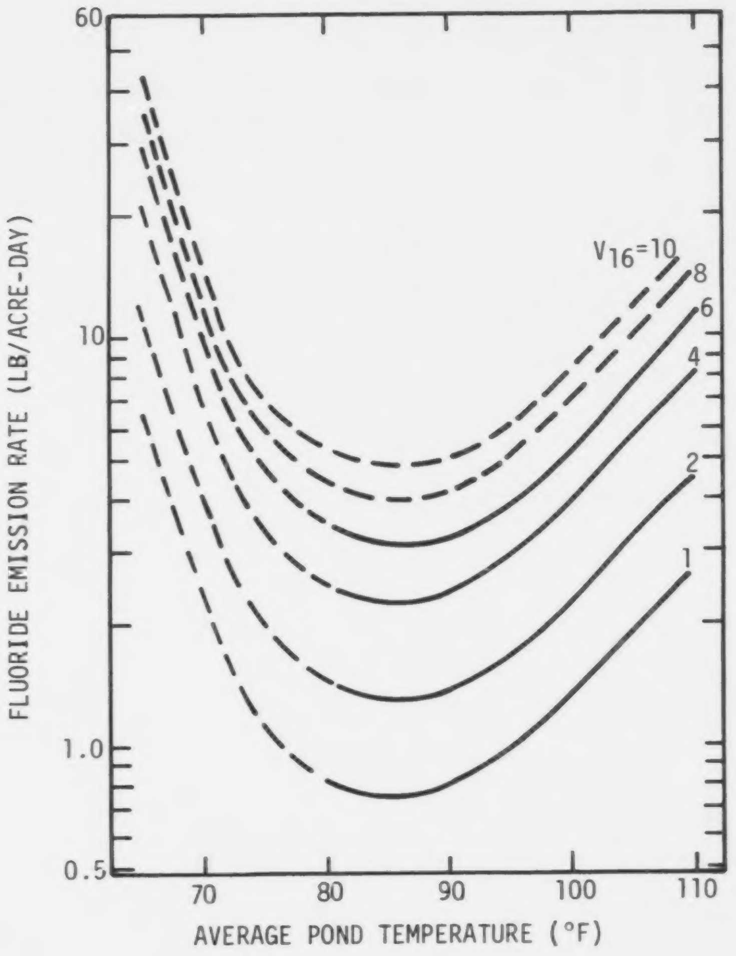

Figure 6-5: Fluorine Emission Rates for Ponds with Water Containing 0.628 g moles/liter Fluorides V_{16} = Wind Speed at 16 Meters in Meters per Second (7)

TABLE 6-4. COMPARISON OF PREDICTED EMISSION FACTORS AT VARIOUS TEMPERATURES (1)

	Surface Wind Speed - M/Sec		
Pond Temperature - °F	0.25	0.54	1.2
75			
Process Water Study	0.41	0.86	1.9
Gypsum Ponds Study	0.96	1.6	2.9
85			
Process Water Study	0.52	1.1	2.4
Gypsum Ponds Study	0.75	1.3	2.2
95			
Process Water Study	1.50	3.2	7.3
Gypsum Ponds Study	0.92	1.6	2.8

The data collected by the remote sensing method indicated that fluoride emission from the gypsum ponds consisted almost entirely of HF; the SiF_4 concentration was below the detectable threshold of about 0.5 ppb.

The fluoride concentrations obtained by the two methods using different principles were in the same order of magnitude. Downwind concentrations during most of the runs were in tens of ppb while the upwind values were from zero to 10 ppb. Vertical traverses indicated that the maximum fluoride concentration was at 15 meters (probably due to local topography) and that the concentration ceiling was at about 25 meters during the tests. Average fluoride emission rates from the gypsum pond were estimated to be in the range of 0.2 to 713 lb/acre-day during the testing period. Measurement of ground level fluoride concentration downwind from the ponds at the W.R. Grace plant showed somewhat lower values than at CF Industries, probably due to lower fluoride concentration in the pond water. The ROSE system proved to be a powerful tool for the measurement of fluoride concentrations at the gypsum pond and the methodology is applicable to similar measurement problems. The system gives essentially real time results requiring no sample handling, which makes it ideally suited for the measurement of fugitive emissions. An additional advantage over standard wet sampling/analysis in this application is that it can distinguish between HF and SiF_4 and can measure the concentration of both species.

6.4 Seepage from the Gypsum Pond

In addition to fluoride emissions into the atmosphere, leaching presents another important environmental problem.

Increased or decreased control of gaseous water-soluble fluorides will not change the amount of liquid waste generated by the fertilizer industry. Most present control systems use pond water for scrubbing, thereby eliminating the creation of additional effluent. The pond water is reused and a discharge is needed only when there is a rainfall in excess of evaporation (8). Figure 6-6 shows a typical gypsum pond system. Natural soil from the surrounding area provides the base for dikes. Gypsum is used to increase the height of the dike. A drainage ditch surrounds the perimeter of the area to control contaminated water seepage through earth and gypsum.

Although the magnitude of subterranean seepage and the potential migration of dissolved fluoride, phosphate and uranium into aquifers is a major environmental concern, virtually no published accounts are available that quantify these distribution patterns. This constitutes, therefore, one of the most poorly resolved facets of fluoride distribution in storage ponds.

Percolation rates through compacted aged gypsum cake and the underlying clayed sediments have been reported to be exceedingly low (9). It was concluded that contamination of deep aquifers is not occurring. On the other hand, some local contamination of the water table aquifer is occurring at some sites. This takes place in the immediate vicinity of the gypsum stacks and ponds. The seepage

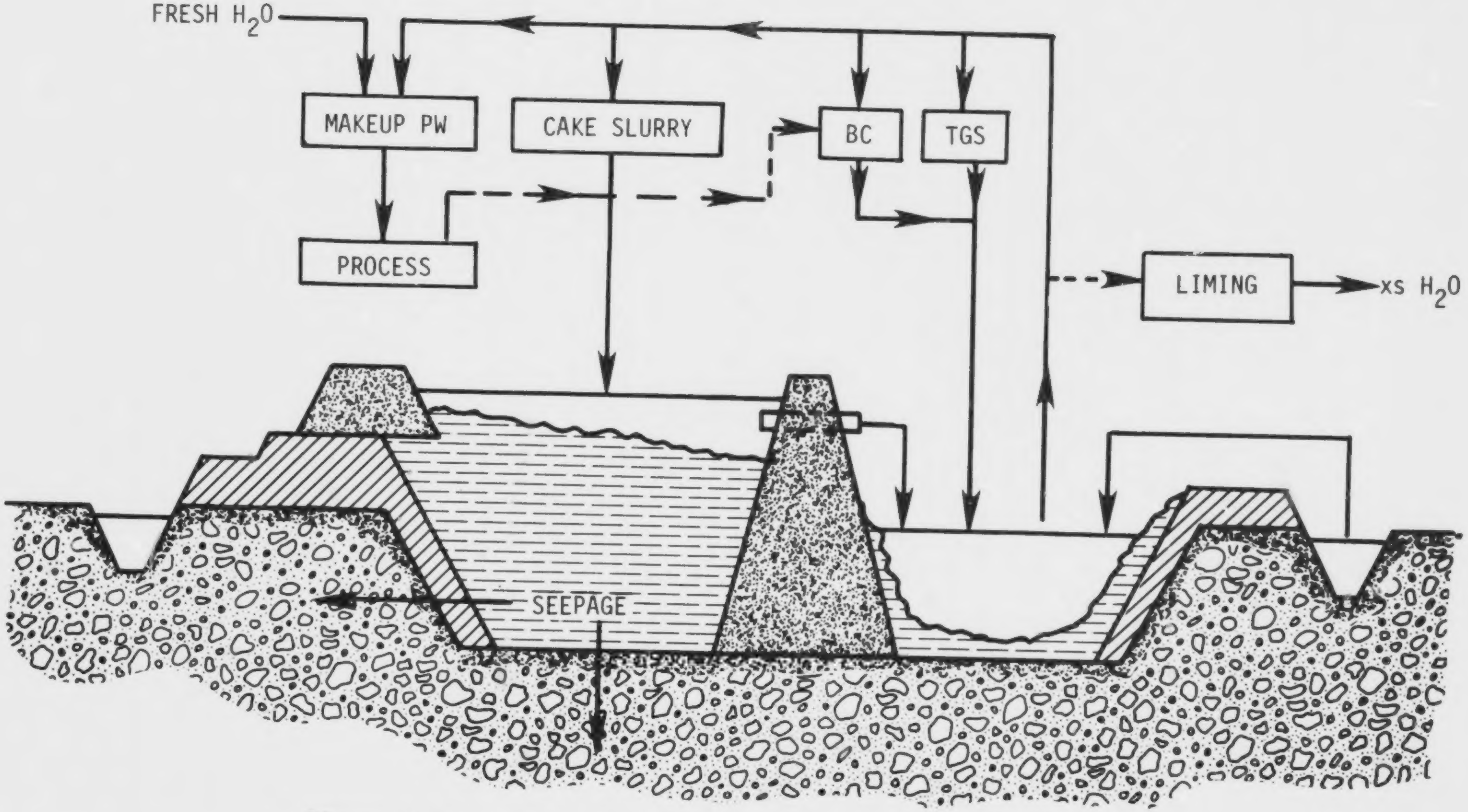
FRESH H_2O
MAKEUP PW
CAKE SLURRY
BC
TGS
PROCESS
LIMING
xs H_2O
SEEPAGE

Figure 6-6: The Storage Pond System: Interrelation of Fluorine Distribution and Water Management (2)

through relatively pervious surface sands frequently reaches open bodies of water such as creeks, rivers and lakes, but this is a seepage problem that is usually relatively easy to contain and control. One potentially serious problem regarding the seepage is that gypsum pond water is highly radioactive. A concentration of 60-100 picocuries per liter (p Ci/l) has been measured which exceeds by at least two to three times the Atomic Energy Commission (AEC) standards for discharge to an unrestricted environment (10).

The State of Florida Department of Environmental Regulation is currently conducting a study at three phosphate fertilizer plants to determine distribution of contaminants around the gypsum pond. Soil samples will be taken through holes located along a line normal to the stack and located at distances of approximately 75, 100, 250, 500 and 1,000 feet from the zero reference point at the gypsum stack-cooling pond-seepage ditch system. The samples will be analyzed for fluoride, total phosphorus and radium 226. Ground water samples will be collected in piezometers and will also be analyzed for fluoride, phosphorus, radium 226 and pH.

6.5 Present Control of Gypsum Pond Emissions

EPA effluent limitation guidelines require that any gypsum pond water discharged to navigable water when rainfall exceeds evaporation meet the limitation shown in Table 6-5. These limitations were maintained as best conventional pollutant control technology (11). Beginning July 1, 1977 and effective when each plant's wastewater discharge permits are subject to renewal, discharge of process wastewater pollutants to navigable waters is allowed only under certain conditions (8).

A two stage liming combined with settling is sufficient control to meet regulations shown in Table 6-5. A flowsheet for a two-stage lime treatment plant is shown in Figure 6-7. At least two stages of liming are required; the first treatment raises the pH from less than 2 to about 3.5 -4.0. The rationale for liming the gypsum ponds to control fluoride emissions is illustrated in Figure 6-8. An increase in pH results in the dissociation of HF making the fluoride ion available for reaction and reduces the concentration of volatile HF cations (1). The equilibrium:

$$Ca^{+} + 2F^{-} \rightleftharpoons CaF_2$$

can be a key in controlling fluoride concentration in ponds without liming since gypsum is near saturation in the pond waters, thereby providing excess calcium ion.

In isolated cases where details of the precipitation mechanisms were identified through precise solid-phase characterizations (unpublished TVA data), the phase chemistry within the pH range of interest (3-9) was found to deviate markedly from the predicted thermodynamic model systems. These comparisons are summarized in Figure 6-9 (2).

TABLE 6-5. EPA EFFLUENT LIMITATIONS GUIDELINES FOR GYPSUM POND WATER (8)

Aqueous Waste Constituent	Maximum Daily Concentration (mg/l)	Maximum Average Of Daily Values For Periods Of Discharge Covering 30 Consecutive Days (mg/l)
Phosphorous as (P)	105	35
Fluoride as (F)	75	25
Total suspended nonfilterable solids	150	50

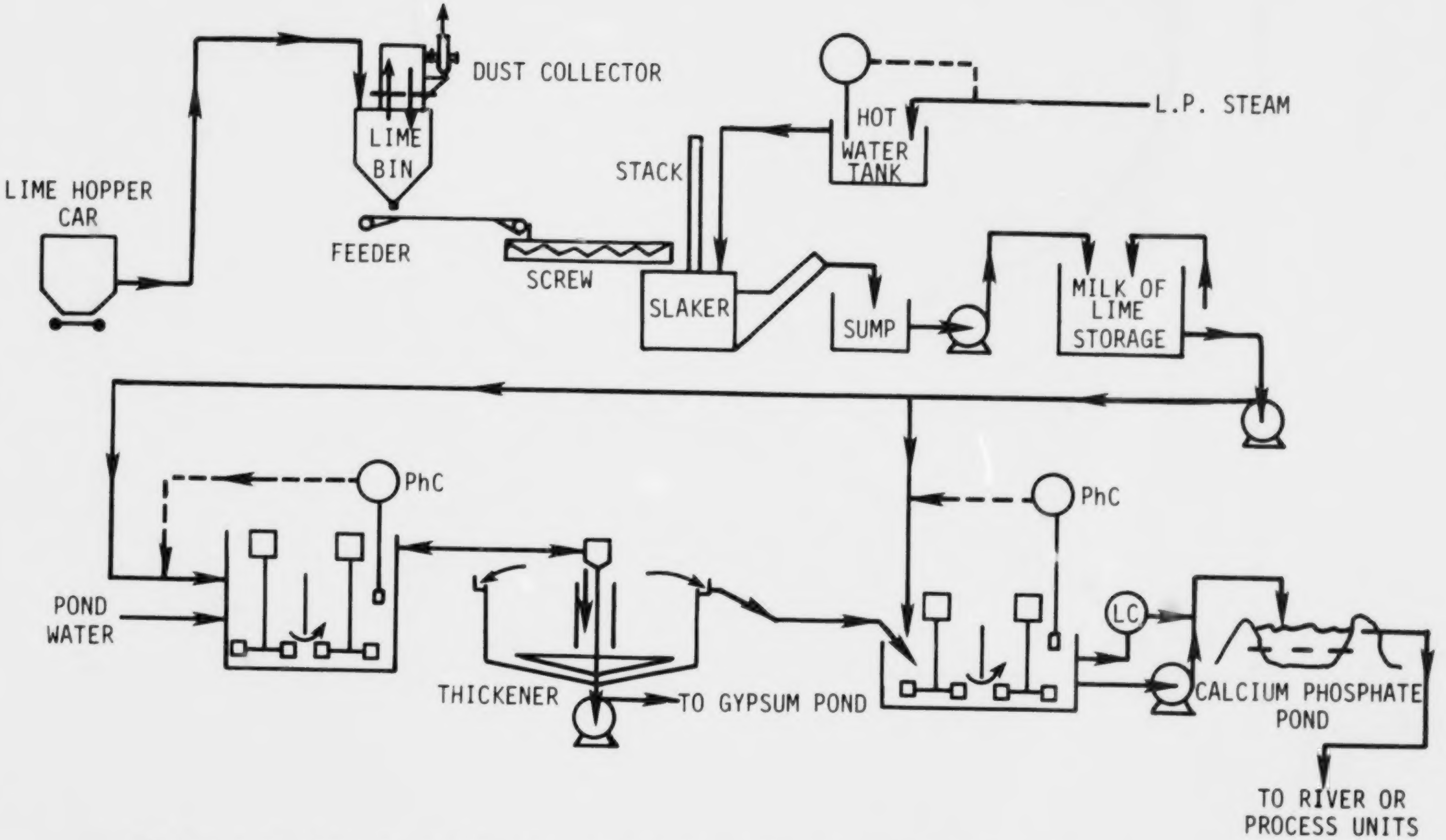
LIME HOPPER CAR
DUST COLLECTOR
LIME BIN
FEEDER
SCREW
STACK
SLAKER
HOT WATER TANK
L.P. STEAM
SUMP
MILK OF LIME STORAGE
PhC
POND WATER
THICKENER
TO GYPSUM POND
PhC
LC
CALCIUM PHOSPHATE POND
TO RIVER OR PROCESS UNITS

Figure 6-7: Flowsheet, "Double Liming" Treatment of Gypsum Pond Water (12)

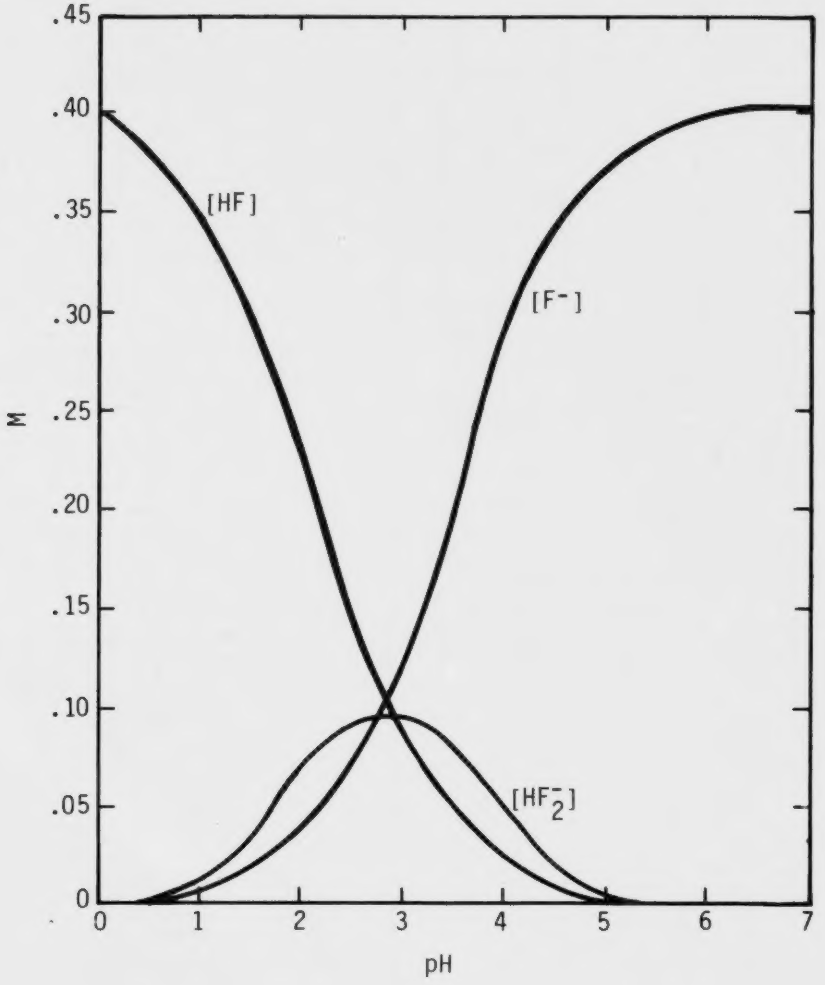

Figure 6-8: Species Predominance Diagram for 0.4 M HF Solution (1)

MODEL PHASE SYSTEMS	PREDICTED SOLIDS
$HF-CaO-H_2O$	CaF_2
$CaO-P_2O_5-H_2O$	DCP, OCP, APATITE
$HF-CaO-P_2O_5-H_2O$	F-APATITE + CaF_2

OBSERVED SOLIDS

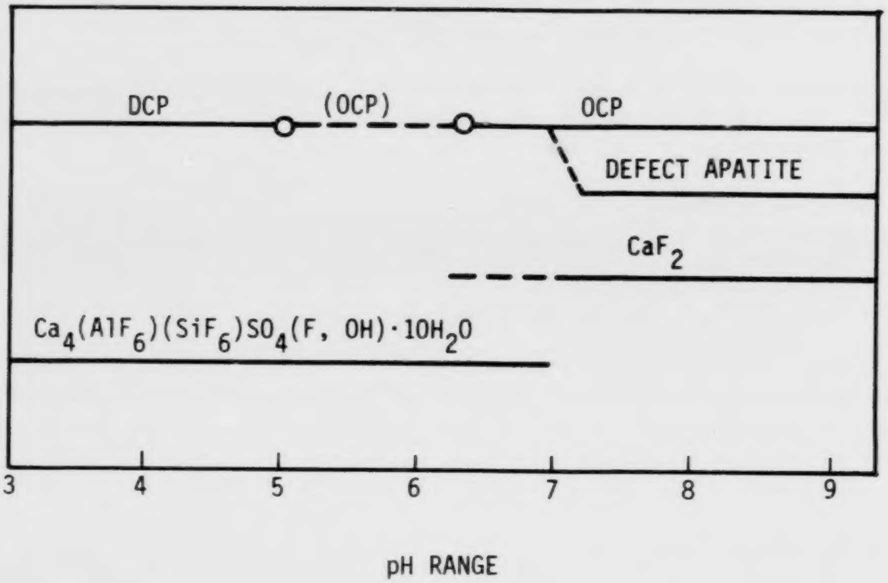

Figure 6-9: Chemical Models of F and P_2O_5 Removal by Lime (2)

The main disadvantage of the liming operation for continual use is the high cost involved. Because the buffering capacity of the gypsum pond water is high at pH 1.0 to pH 3.0, large amounts of lime are required to raise the pH initially to 3.0 relative to the amount required to raise the pH from 3.0 to 6.0 (1). An additional disadvantage is the deposition of calcium fluoride on the lime particles, rendering them chemically inactive. The use of high intensity agitators is required to prevent this. It is also important to note that radium 226 is also precipitated by lime treatment with increasing pH.

6.6 Identification of Control Techniques For Gypsum Ponds

As seen in previous sections, the gypsum pond is plagued with two emissions that are presently uncontrolled: fluoride emissions into the atmosphere and contaminant seeping into the water table aquifer. The obvious answer to preventing these emissions is not to use ponds for fluoride removal and water cooling. This approach is unfortunately prohibitively expensive and can be used only in isolated cases, such as the Mississippi chemical plant in Pascagoula.

The purpose of this section is to review the available control processes for reducing fluoride emissions from gypsum ponds. The following control options will be briefly considered:

1. Two pond system
2. Kidde process
3. Swift process
4. Liming of cooling ponds
5. Dry conveyance of gypsum to stacks
6. Phosphate rock calcining
7. Change to hemi/dihydrate process
8. Use of algae
9. TESI dry system.

6.6.1 Two Pond System

The reasons for separate gypsum/cooling ponds given in Reference (1) are:

- The required size of the gypsum slurry pond is small (about 5 acres) since no area is required for cooling. This water would be the most contaminated and acidic water in the plant due to the presence of P_2O_5, H_2SO_4, iron and aluminum complexes, and fluorides from the filtration operation.

- The size of the pond required for the barometric condensers is determined by the cooling requirements. This area is estimated to be 0.1 acre/TPD P_2O_5.

Figure 6-10 shows the flow diagram for a two pond system (1). One pond would service the filtration operation by receiving gypsum slurry. The other pond would receive waters from the fume scrubbers, flash coolers and the evaporation trains. The cooling ponds would require about 200 acres for a 1,000 TPD P_2O_5 plant while the gypsum pond would require approximately 5 acres. The costs required to segregate the two ponds are considered negligible compared to other control costs. Pond segregation is considered tantamount in applying control options 2 through 5.

6.6.2 Kidde Process

The Kidde process is used to defluorinate wet-process phosphoric acid and convert the extracted fluorine into various fluorine compounds. Fluorine compounds that may be produced include aluminum fluoride, sodium aluminum flouride (cryolite), hydrogen fluoride and calcium fluoride (fluorspar).

The basic reaction in the Kidde process occurs between reactive silica and hydrogen fluoride producing silica tetrafluoride. SiF_4 is then condensed and reacted with bifluoride. Barometric condenser and scrubber water is combined and neutralized with ammonia, and the product, ammonium silicofluoride, is then stored for shipment or reacted further to produce additional products, with aluminum fluoride being the principal salable byproduct. The approximate fluoride reduction in the Kidde process is about 95%. The major benefits of the process are (1):

- Reduction or elimination of liming for pond water discharged from the plant's cooling ponds.
- Improvement in the physical properties of the phosphoric acid due to a reduction in its fluorine content.
- Increased recovery of fluoride otherwise lost in the evaporation stage.

An economic evaluation indicates that a Kidde process capable of servicing a 1,000 TPD P_2O_5 facility would cost approximately 9.3 million dollars (1). The total investment is of the same order of magnitude as that required for the P_2O_5 complex itself. No full-scale plant actually exists today or is under construction.

6.6.3 Swift Process

The Swift process involves the removal of fluorine compounds from wet process phosphoric acid manufacturing in a manner similar to the Kidde process.

The vapors from three evaporation units used for concentration of phosphoric acid are scrubbed by an absorber which uses cooling water and removes 90% of the fluorides. The resulting diluted H_2SiF_6 is removed and concentrated in the absorbers in a countercurrent manner resulting in 25% H_2SiF_6 as a final product.

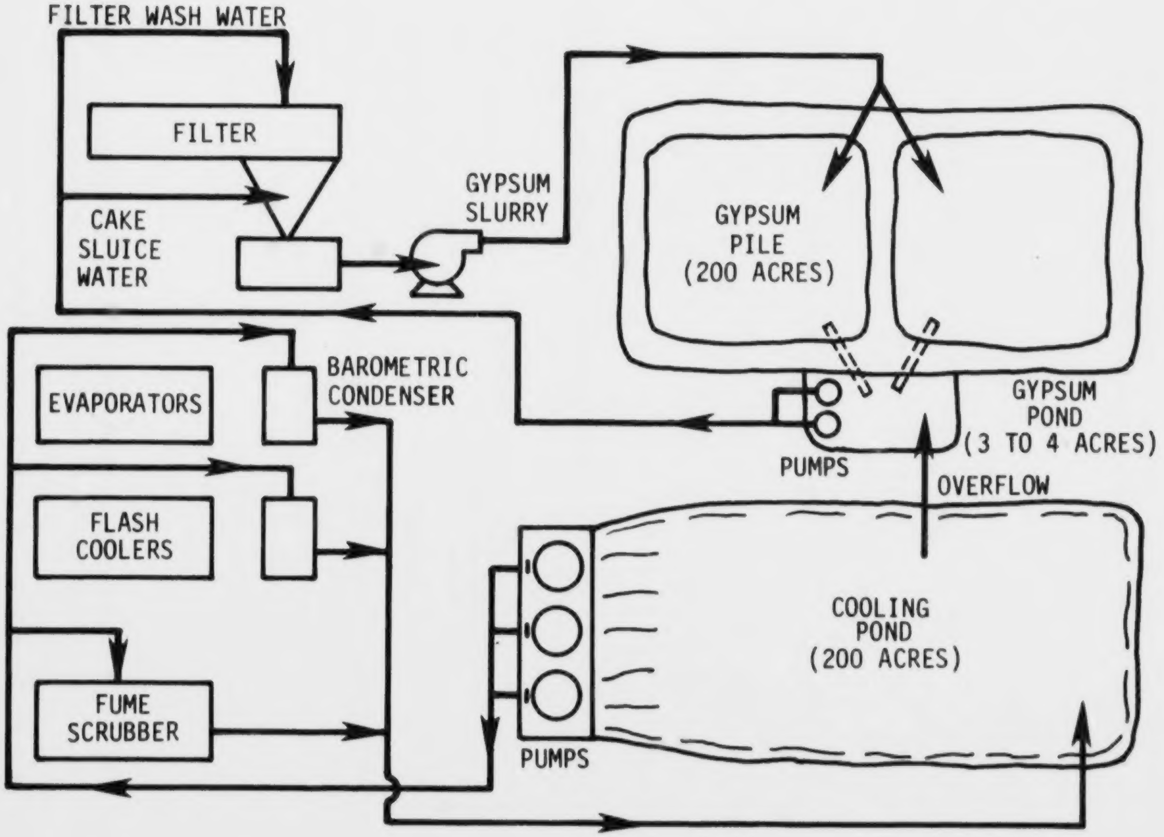
FILTER WASH WATER
FILTER
CAKE
SLUICE
WATER
GYPSUM
SLURRY
GYPSUM
PILE
(200 ACRES)
BAROMETRIC
CONDENSER
EVAPORATORS
FLASH
COOLERS
FUME
SCRUBBER
PUMPS
GYPSUM
POND
(3 TO 4 ACRES)
OVERFLOW
COOLING
POND
(200 ACRES)
PUMPS

Figure 6-10: Two Pond System for Phosphoric Acid Plant (1)

The original purpose of the Swift process was for the economical recovery of byproduct fluorides, but when coupled with a two pond system it is now recommended as a pollution control system. The cost of retrofit to an existing plant is $500,000 for the equipment servicing each evaporator or $1,500,000 total capital investment for three modules (1). If all fluosilicic acid produced can be sold, which is doubtful, the Swift process can operate at a profit.

6.6.4 Liming of the Cooling Pond

If gypsum and cooling ponds are segregated, the latter will contain fluorides and small amounts of P_2O_5. Thus it is necessary only to add significant lime to precipitate out fluoride compounds as fluorspar. In bringing the pH of the cooling water from 1.4 to 3.9, the emission of fluorides can be reduced by 90%. This can be achieved by single stage liming shown in Figure 6-11. It will be necessary to lime the pond only once and thereafter to add sufficient lime to handle the theoretical amount of fluorides entering the cooling pond. The pond with an initial pH of 1.4 will need the addition of 0.157 lb/gallon to reduce fluoride emissions by 90% (1).

Installation of a single-liming system at existing plants should pose few problems since most of them presently use double liming for pond water overflow discharges.

During steady state operation 135 lb CaO per ton P_2O_5 will be required. Since a relatively large quantity of lime is required, it will be more economical for the plant to produce its own lime from limestone. Total approximate annualized costs using this strategy will result in an estimated cost increase of $3/ton P_2O_5.

6.6.5 Dry Conveyance of Gypsum to Stacks

Transporting the gypsum to stacks using a dry conveyor belt rather than a slurry pipeline could reduce the fluoride emissions. The benefits/disadvantages are not as easily determined as the annual costs are calculable. Apparently it is economically justified where the gypsum can be marketed for agricultural or other uses.

Annualized operating costs of approximately $1.4/ton P_2O_5 were estimated (1).

6.6.6 Phosphate Rock Calcination

Defluorination of phosphate rock through precalcination prior to acidulation with sulfuric acid occurs in two regimes. At low temperatures (up to 2000°F) 66% of the fluorine is removed, while heating to fusion temperature (2500°F) achieves 90% removal. The off-gases must be scrubbed, which is a major disadvantage of this option, making the economics very unattractive.

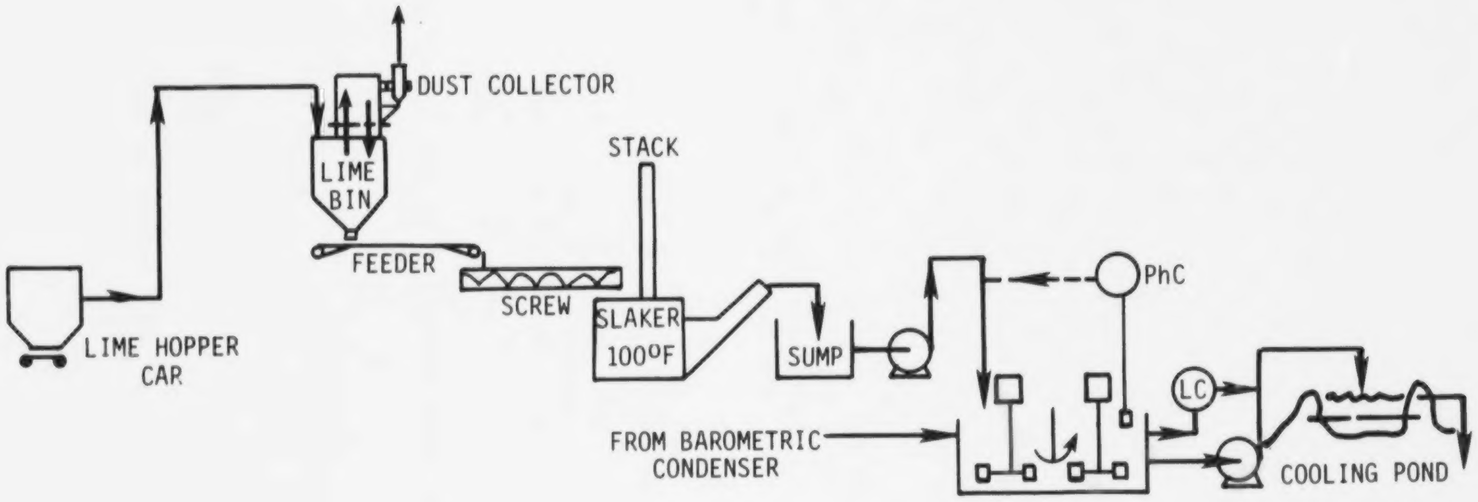
DUST COLLECTOR
LIME BIN
STACK
FEEDER
SCREW
SLAKER 100°F
SUMP
PhC
LC
LIME HOPPER CAR
FROM BAROMETRIC CONDENSER
COOLING POND

Figure 6-11: Proposed Single Liming System (1)

6.6.7 Change to Hemi/Dihydrate Process

The hemihydrate-dihyrate process for making wet-process phosphoric acid has been in use in Japan for several years. Its primary advantages are the higher overall yield of P_2O_5 and the production of high quality gypsum, suitable for gypsum plaster and gypsum boards. About 40% of the fluorides present in the rock are volatilized in the acidulation stages and may be recovered as fluosilicic acid.

The variations of this process differ from the common dihydrate process in that hemihydrate is formed during decomposition of rock and is recrystallized as dihydrate before filtration. It is estimated that 70-95% of the fluorides can be recovered as H_2SiF_6.

In order to use the hemi/dihydrate process, the existing plants would have to be extensively changed and markets found for the gypsum and fluosilicic acid produced. The economics with low cost U.S. rock are questionable.

6.6.8 Use of Algae

Initial work with algae indicates that the pH can be increased to 3 and the fluoride concentration decreased by a factor of 2 to 7 within 3 hours. Higher plant life, such as Juncus and autotrophic bacteria have given indications of providing a similar effect (4).

This option is at the for scientific feasibility evaluation stage.

6.6.9 TESI Dry System (4)

In this process the gaseous fluorides are removed at elevated temperatures by a dry chromatographic technique (TESISORB). Fine particulate is also collected in a dry reactor. Since no cooling is required, a heat load normally imposed on the pond is circumvented.

The cost of TESISORB is \$0.07/ton P_2O_5. The capital cost for the hardware is estimated to be one-half of the cost for wet scrubbing.

Testing recently completed by EPA of the TESI dry system at a secondary aluminum installation demonstrated good performance. Several secondary aluminum plants now use this system which might be applicable to fertilizer plants. A recommended demonstration project will be described in Section 9.

6.6.10 Comparison of Control Options

The cost and efficiency of control options 2 through 6 is shown in Table 6-6.

The Swift process appears to be the most cost-effective method in conjunction with a segregated two pond system. The economics of this process depend on the H_2SiF_6 market. Process complexity is another obstacle to its commercialization.

The second most cost effective method involves liming the pond waters to pH 4. The advantage of this option is its simplicity. The disadvantages are connected with secondary environmental impact caused through handling of large quantities of limestone.

The Kidde process has the highest potential recovery and the greatest technical merit. Unfortunately, the high annualized cost and process complexity makes its application rather dubious. The other three processes suffer from the disadvantage of needing major plant changes and none is currently used on a large scale in the U.S.

The use of algae looks interesting but needs more research before it can be considered as an engineering option.

The TESI dry system has been successfully demonstrated in the secondary aluminum industry and a demonstration of this method in a phosphate fertilizer plant is proposed.

6.7 References

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TABLE 6-6. CAPITAL INVESTMENT AND OPERATING COSTS FOR FLUORIDE CONTROL OF 1,000 TPD P_2O_5 PLANT (1)

Process	Where Applied	Fluorine Removal Efficiency	Total Capital Investment $MM	Annualized Operating Costs Total, MM	Annualized Operating Costs $/Ton P_2O_5	By-Product
Kidde	Barometric Condensers	95-98%[a]	2.57	2.31	7.46	$(NH_4)_2SiF_6$
Swift Absorption	Barometric Condensers	90%[b]	1.30	0.17	1.25[c]	H_2SiF_6
Liming	All Cooling Pond Water	90%[b]	2.10	0.97	3.13	None
Conveyor	Gypsum Filter After Acidulation	a	1.07	0.43	1.40	None
Pre-Calcination of Rock	Crushed Phosphate Rock	b	29.81	7.57	24.42	None

[a] Not calculated due to uncertainties in Fluorides evolved from filter cake.

[b] 90% removal of fluoride in rock is achieved. However, the fluorides evolved are scrubbed and transferred to ponds.

[c] A credit of $2.26/ton P_2O_5 is realized if all fluorilicic acid produced is sold at $60/ton (100% H_2SiF_6).

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7.0 SOLID WASTE CONTROL

7.1 Sources and Amount of Solid Waste

There are three sources of solid waste in the phosphate fertilizer industry (1):

- Gypsum from the filtration of wet process phosphoric acid
- WPPA sludge
- Wet scrubber liquor

The quantity of gypsum produced in a WPPA plant ranges from 4.6 to 5.2 metric tons of gypsum/metric ton P_2O_5; therefore, approximately 1,360 m^3 of gypsum will be accumulated yearly per metric ton of P_2O_5 produced per day (2).

A second source of solid residue is phosphate rock from clarifiers (sludge). Effluent from clarifiers ranges from 0.7 m^3 to 3.2 m^3/metric ton P_2O_5 (3).

The third source of solid waste is the liquor from wet scrubbers which are used throughout the phosphate fertilizer industry. At ammonium phosphate plants, scrubber liquor piped to the gypsum pond contains about 10 g of solid waste (consisting primarily of silicon hydroxide) per kilogram P_2O_5.

7.2 Special Waste Regulation (4)

As a result of wind and water erosion, the large piles of by-product gypsum in the vicinity of WPPA plants serve as sources of airborne and waterborne emissions for years after the time of abandonment. Furthermore, these piles contain thousands of curies of radium 226 in a readily leachable form (5). The piles are sources of low radioactivity and EPA has addressed them under Resource Conservation and Recovery Act (RCRA) regulations. These regulations are controversial and opposed by the industry.

In the course of preparing its hazardous waste regulations under Subtitle C of RCRA, EPA realized that some portions of certain very large volume wastes would come within the purview of the regulatory scheme. These wastes include cement kiln dust, utility waste (fly ash, bottom ash, and scrubber sludge), phosphate mining and processing waste, uranium and other mining waste, and gas and oil drilling muds and oil production brines.

The Agency has very little information on the composition, characteristics, or the degree of hazard posed by these wastes. Nor does the Agency yet have data on the effectiveness of current or potential waste management technologies or the technical or economic practicability of imposing the proposed RCRA standards on facilities managing such waste.

The limited information EPA does have indicates that such waste occurs in very large volumes, that the potential hazards posed by the waste are relatively low, and that the waste generally is not amenable to the control of techniques developed under the proposed RCRA §3004 regulations. The Agency is calling such high-volume hazardous waste "special waste" and is proposing to regulate it with special standards.

Table 7-1 provides some information about those wastes which, when hazardous, EPA proposes to regulate with special standards. With two exceptions, EPA does not know how much of the total amount of waste generated in these categories is, in fact, hazardous and thus subject to Subtitle C regulations. Only waste which is "hazardous" as defined under EPA's §3001 rules , however, will be treated as "special waste." Any portion of the waste on the following table which is not hazardous under the §3001 standards is not regulated at all under Subtitle C of RCRA and thus is not "special waste."

Under EPA's proposed "special waste" regulations, the treatment, storage and disposal of phosphate fertilizer solid waste will have to be managed in accordance with standards set forth in Section 250.46-3 which provides as follows:

(a) The treatment, storage, and disposal of hazardous waste listed below (and which is listed as hazardous waste in 250.14 of Subpart A) are subject to the requirements specified in paragraphs (b) and (c):

(1) Overburden, slimes (phosphoric clays) and tailings from phosphate rock mining;

(2) Waste gypsum from phosphoric acid production; and

(3) Slag and fluid bed prills from elemental phosphorus production.

(b) The requirements of the following Sections of the proposed 3004 standards are applicable to waste listed under paragraph (a):

250.43(f) (General Facility Standards--waste analysis);

250.43-1 (General Site Selection--for new sources only);

250.43-2 (Security);

250.43-5(a), (b)(1), (b)(2)(i), (b)(6), and (c) (Manifest System, Recordkeeping, and Reporting);

250.43-6 (Visual Inspections);

250.43-7(1), and (m) (n) (Closure and PostClosure); and

250.43-8(a), and applicable requirements of (c) and (d) which relate to groundwater monitoring, (Groundwater and Leachate Monitoring-for groundwater monitoring only).

TABLE 7-1. SPECIAL WASTE (Metric tons/yr) (4)

Waste	Quantity	Possible Hazard
Cement Kiln Dust	12 million*	Alkalinity and heavy metals
Utility Waste (fly ash, bottom ash, scrubber sludge)	66 million*	Heavy metals (trace)
Phosphate Mining, Beneficiation, and Processing Waste	400 million	Radioactivity (low levels)
Uranium Mining	150 million	Radioactivity
Other Mining Waste	- billion	Heavy metals, acidity
Gas and Oil Drilling Muds and Oil Production Brines	5 million	Alkalinity, heavy metals, toxic organics, salinity

*Hazardous waste portion unknown.

(c) Additionally, the following requirements are applicable to waste listed under paragraph (a):

(1) Location of waste deposits shall be recorded on reference maps which shall be maintained through the operating and post-closure periods.

(2) Land reclaimed by filling with waste listed in paragraph (a) shall be used for residential development only where provisions have been made to prevent alpha radiation exposure from Radon 222 inhalation from exceeding background levels by 0.03 Working Level Units and gamma radiation from exceeding background levels by 5 micro Roentgens/hour. The possible need for special construction methods for structures on such reclaimed land shall be identified to any future land owner(s) by recording a stipulation in the deed of the reclaimed land.

(3) Building products manufactured from waste listed in paragraph (a) shall not be used if such products cause alpha radiation exposure from Radon 222 inhalation to exceed background levels by 0.03 Working Level Units or cause gamma radiation to exceed background levels by 5 micro Roentgens/hour. Purchasers of waste and of products manufactured from waste shall be advised of this requirement by the seller.

(4) Analysis required under §250.43-8(c)(5) shall also include determination of Radium concentration in picocuries/gram.

(5) Analysis required under §250.43-8(c)(6) shall also include the following:

(i) Radium, picocuries/gram
(ii) Phosphate, mg/liter
(iii) Fluoride, mg/liter

7.3 Phosphate Fertilizer Solid Waste Control

The solid waste originating from the three sources discussed in Section 7.1 can be disposed in three ways (1):

1. Gypsum ponds and piles
2. Abandoned mine pits
3. Sea disposal

In the United States, more than 90% of the plants use gypsum ponds. As one gypsum pond becomes filled, the gypsum slurry stream is diverted to another area and the original pond is dried. The resulting gypsum piles range in height from 30 to

36 meters. The disposal of gypsum in abandoned mine pits is practiced in Central Florida. The only environmental hazard associated with such disposal is leaching of fluorides, phosphates and radium 226 in the aquifer. Since mine pits are closer to the subsurface of the aquifer, a leaching hazard is greater than that found in gypsum ponds.

Sea disposal is mostly practiced in foreign countries while less than 2% of U.S. plants use it.

For every ton of phosphoric acid produced from phosphate rock, about five tons of waste gypsum are generated. Since most of the gypsum is disposed of through a gypsum pond-pile system, the stacking technology will be discussed next.

Planning of a gypsum stack and acid water system is as important as the detailed engineering design (6). Figure 7-1 shows a planning flowchart for gypsum stack and pond design illustrating necessary steps and their interrelations. The first step is the establishment of the process and climatic constraints. Process constraints include production estimates, plant and stack life, process water temperature, etc. Climatic constraints may influence process constraints, in particular heat and water balances.

Sizing of the stack and pond takes place in the next step. The area required for the gypsum stack is dictated by its design maximum height. After the sizing a field investigation should be carried out of the subsurface condition of a tentative site. The final selection of the site can be made in a rational manner by weighing the engineering pros and cons of each site. In designing a gypsum pond-stack system, one can use an idealistic layout based on experience as described in Reference (6). The following features have been included in this idealistic layout:

1. The gypsum stack is square in plan.
2. Two gypsum ponds are used. One is active while the other one is drained.
3. The acid water cooling pond and surge area is built entirely around the perimeter of the gypsum stack.
4. An exposed clay starter dike is used.
5. An internal drainage system is used to control seepage.
6. The decant structures are used in the center of the divider dike so that the finer gypsum settles at the center of the stack around the decant structure.

The detailed engineering design of the gypsum pond-stack system is described in Reference (6). The major environmental concern regarding the gypsum pond-stack system is groundwater contamination. This problem was discussed in Section 6 with a conclusion that, pending the results of ongoing field programs, contamination is probably limited to the water table aquifer.

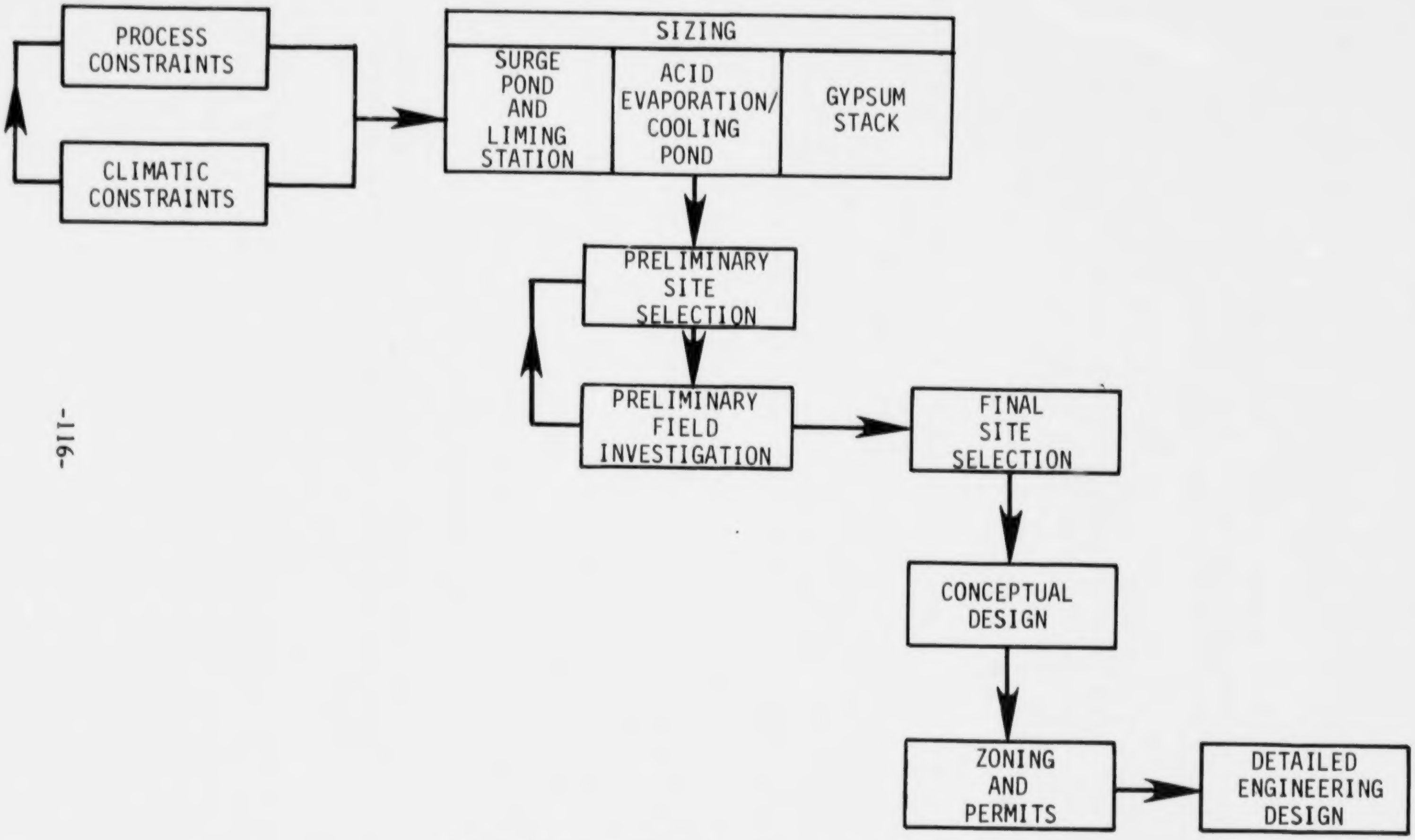

PROCESS CONSTRAINTS
CLIMATIC CONSTRAINTS
SIZING
SURGE POND AND LIMING STATION
ACID EVAPORATION/ COOLING POND
GYPSUM STACK
PRELIMINARY SITE SELECTION
PRELIMINARY FIELD INVESTIGATION
FINAL SITE SELECTION
CONCEPTUAL DESIGN
ZONING AND PERMITS
DETAILED ENGINEERING DESIGN

Figure 7-1: Gypsum Stack and Acid Water System (6)

An important question regarding phosphate fertilizer solid waste is the possibility of resource recovery. The gypsum has been used in the United States on calcium-deficient soils, alkali soils and for land reclamation. In Europe and Japan relatively pure gypsum obtained from the hemihydrate process is successfully used for wallboard production.

While several potential resource recovery methods are technically feasible, less than 1% of the gypsum waste in the United States is utilized because its recovery is not economically feasible.

7.4 References

1. Nyers, J.M., et al, Source Assessment: Phosphate Fertilizer Industry, EPA 600/2-78-004, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1978, 185 pp.

2. Lutz, W.A., Pratt, C.J., Principles of Design and Operation. In: Phosphoric Acid, Volume I, Slack, A.V. (ed.), Marcel Dekker, Inc., New York, NY, 1968. pp. 158-208.

3. Martin, E.E., Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Basic Fertilizer Chemicals Segment of the Fertilizer Manufacturing Point Source Category. EPA 440/1-74-011-e (PB-238 652), U.S. Environmental Protection Agency, Washington, D.C., March 1974, 170 pp.

4. Proposed §3004 rules under the Resource Conservation and Recovery Act (40 CFR 250, Subpart D, 43 FR 58991), December 18, 1978.

5. Reconnaissance Study of Radiochemical Pollution from Phosphate Rock Mining and Milling, U.S. Environmental Protection Agency, Office of Enforcement, Denver, Colorado, December 1973, 45 pp.

6. Wissa, A.E.Z., Gypsum Stacking Technology, Presented at 1977 Annual Technical Meeting, Central Florida and Peninsular Florida Sections, American Institute of Chemical Engineers, Clearwater, Florida, May 1977, 44 pp.

8.0 REVIEW OF CONTROL EQUIPMENT VENDORS AND ENGINEERING FIRMS

Sections 5 and 6 discussed various air and water control techniques and equipment but no specific mention of any vendors was made. The wastewater treatment design is done by local engineering and consulting firms and the plants themselves.

Since all phosphate fertilizer processes use scrubbers for air emission control, the discussion will be limited to scrubber vendors. Contacts with the phosphate fertilizer industry revealed that a large number of vendors have their equipment installed and operated in this industry. Since it is beyond the scope of this study to make a complete inventory of pollution control equipment vendors, only four selected vendors will be reviewed. Selection of the following representative vendors was based on discussions with the Industrial Gas Cleaning Institute.

Large installations are represented by:

1. Environmental Elements Corporation
2. The Ducon Company, Inc.

Smaller installations are represented by:

3. The Ceilcote Company
4. Heil Process Equipment Company.

The purpose of this review is to illustrate briefly the type of control equipment furnished by these vendors and the process application. In preparing the discussion on these four scrubber vendors, vendors' bulletins, open literature, discussion with vendors and industry and the McIlvaine Scrubber Manual (1) were used.

8.1 Environmental Elements Corporation (ENELCO), Baltimore, MD

ENELCO is a subsidiary of Koppers Company with annual scrubber sales of $1 to 5 million (1). The company's scrubber expertise has been acquired through acquisition of Poly Con Corporation which is a subsidiary of ENELCO. ENELCO is represented by Nosun Engineering Sales, Inc., Lakeland, Florida which serves as a liaison with the phosphate fertilizer industry. Three major scrubber types manufactured by ENELCO and their principles of operation are shown in Figures 8-1, 8-2, and 8-3 (2). The materials of construction vary with application but the most commonly used are: mild steel, rubber lined steel, FRP and acid brick lined steel.

McIlvaine lists the following design advantages and disadvantages for Venturi and packed towers manufactured by Poly Con which apply to almost all conventional designs (1).

VENTURI

DESIGN ADVANTAGES: The annular type and full throat Venturi have those design advantages common to high energy scrubbers. High efficiency can be

PRINCIPLES OF OPERATION

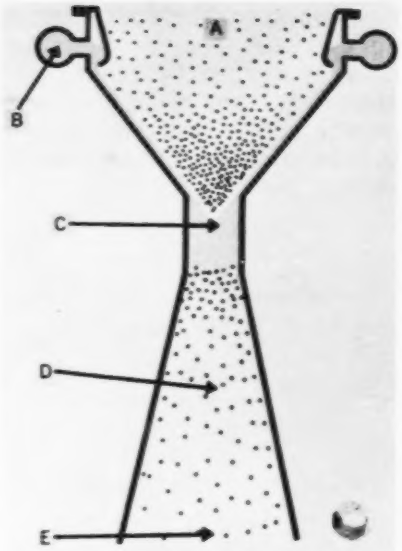
A - The contaminated gas enters the Venturi and is accelerated in the converging section.

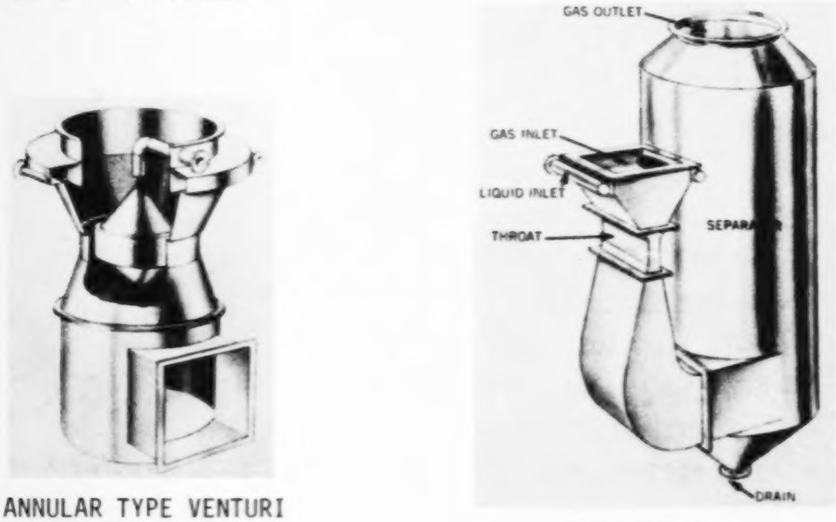
B - The scrubbing liquid is introduced, uniformly, at the top of the converging section and cascades by gravity and velocity pressures towards the throat.

C - The contaminated gas and the scrubbing liquid enter the Venturi Throat where they are mixed at high energy and extreme turbulence.

D - The scrubbed gas and entrained droplets (with contaminants entrapped) enter the diverging section where further collisions and agglomeration take place creating larger drops.

E - The gases then proceed to the separator where all liquid drops are easily removed from the gas stream and collected.





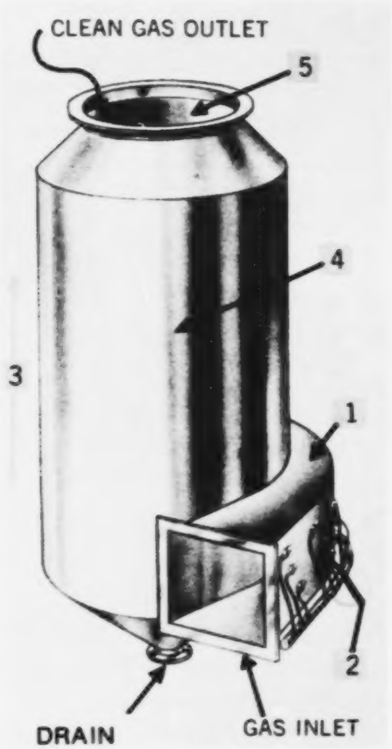
ANNULAR TYPE VENTURI
WITH FLOODED ELBOW

VENTURI WITH
CYCLONIC SEPARATOR

Figure 8-1: Enelco Venturi Gas Scrubber (2)

PRINCIPLES OF OPERATION

The contaminated gas enters the involute section where it is brought into intimate contact with positive curtains of liquid spray. The treated gases proceed along the involute where the bulk of scrubbing liquid is separated. The accelerated gases then enter the spin zone where the remainder of the entrained droplets are removed. The liquid travels by gravity to the bottom cone drain and the cleaned gases leave the scrubber at the top.



1 - INVOLUTE GAS INLET
2 - WALL MOUNTED SPRAYS
3 - REDUCED HEIGHT
4 - NO INTERNALS
5 - LOW PRESSURE DROP

Figure 8-2: Enelco Cyclon-Spray Gas Scrubber (2)

PRINCIPLES OF OPERATION

The contaminated gas enters the bottom of the tower and flows upward through the packed section counter to the scrubbing liquid. The packing forces the gas to follow a tortuous path over the contact surfaces and interstices creating intimate mixing with the descending liquid. The spray nozzles are mounted on retractable manifolds. Demister located over the spray manifolds prevents liquid entrainment. The scrubbing liquid is collected and stored at the bottom of the scrubber.

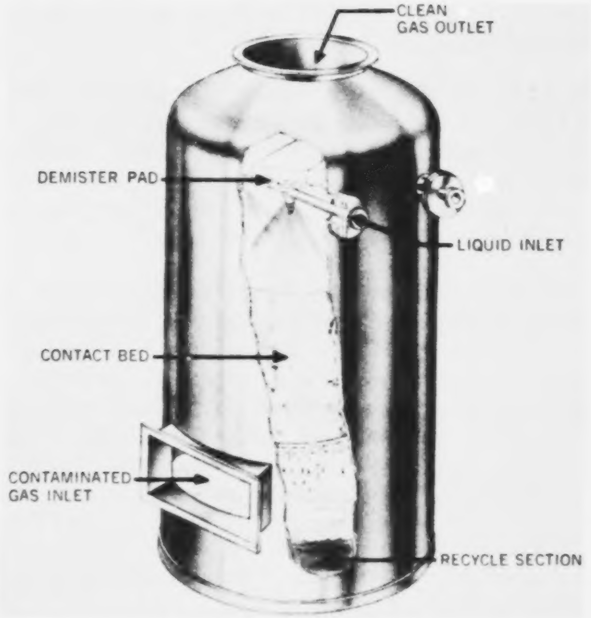

CLEAN GAS OUTLET
DEMISTER PAD
LIQUID INLET
CONTACT BED
CONTAMINATED GAS INLET
RECYCLE SECTION

Figure 8-3: Enelco Poly Pack Tower Gas Scrubber (2)

achieved at some energy expenditure. Pressure drop can be varied in both units. Both types can be combined with the cyclonic type, separator/cooling tower type, and demister type entrainment separators.

DESIGN DISADVANTAGES: These units have the disadvantages common to all Venturi scrubbers. High energy requirements, and potential abrasion of internals due to the high velocity gas stream are the most significant.

PACKED TOWER

DESIGN ADVANTAGES: Like other packed towers these units have relatively high absorption efficiency for the energy consumed. Initial cost is also low compared to other scrubber types.

DESIGN DISADVANTAGES: As in other packed towers scaling can occur easily with precipitation or introduction of particulate.

Figure 8-4 shows a WPPA process schematic with special emphasis on the air emission control system (3). Since the author of the referenced article is now with ENELCO, the pollution control schematic in Figure 8-4 would be representative of ENELCO's approach. The same holds for Figure 8-5, showing an ROP-TSP process schematic with emphasis on air pollution control.

8.2 The Ducon Company, Inc., Mineola, NY

Ducon is a subsidiary of the U.S. Filter Corporation which subsequently acquired MikroPul. MikroPul already had a scrubber group called Airtron with a number of installations in the phosphate fertilizer industry. Since the decision was made to transfer all scrubber activities to Ducon, the Airtron Scrubber design was phased out. Ducon is represented by Linder Industrial Machinery Company, Lakeland, Florida which serves as a liaison with the phosphate fertilizer industry.

Figure 8-6 shows a cyclone, five wet scrubbers, and a brief feature description of typical Ducon units (4). McIlvaine states the following advantages and disadvantages for the scrubbers: The VO Oriclone has a design advantage in that it is a compact, low head room unit. The U.W-4 dynamic scrubber has the design advantage that the wet fan stays clean on some applications where a dry fan would not; however, unit height is a disadvantage. Figure 8-7 shows an Oriclone VVO Venturi which is well suited for use in the phosphate fertilizer industry (4). According to the vendor's bulletin, this scrubber has the following features (4):

1. Simple, trouble-free design--There are no spray nozzles or distribution jets in which solids can collect; therefore, slurries, of any solids content capable of being pumped, can be handled.
2. No wet-dry line build-up--Scrubbing liquid, introduced through open pipes on the internal surface of the convergent section, swirls down in a flow pattern that assures thorough wetting of the complete surface.

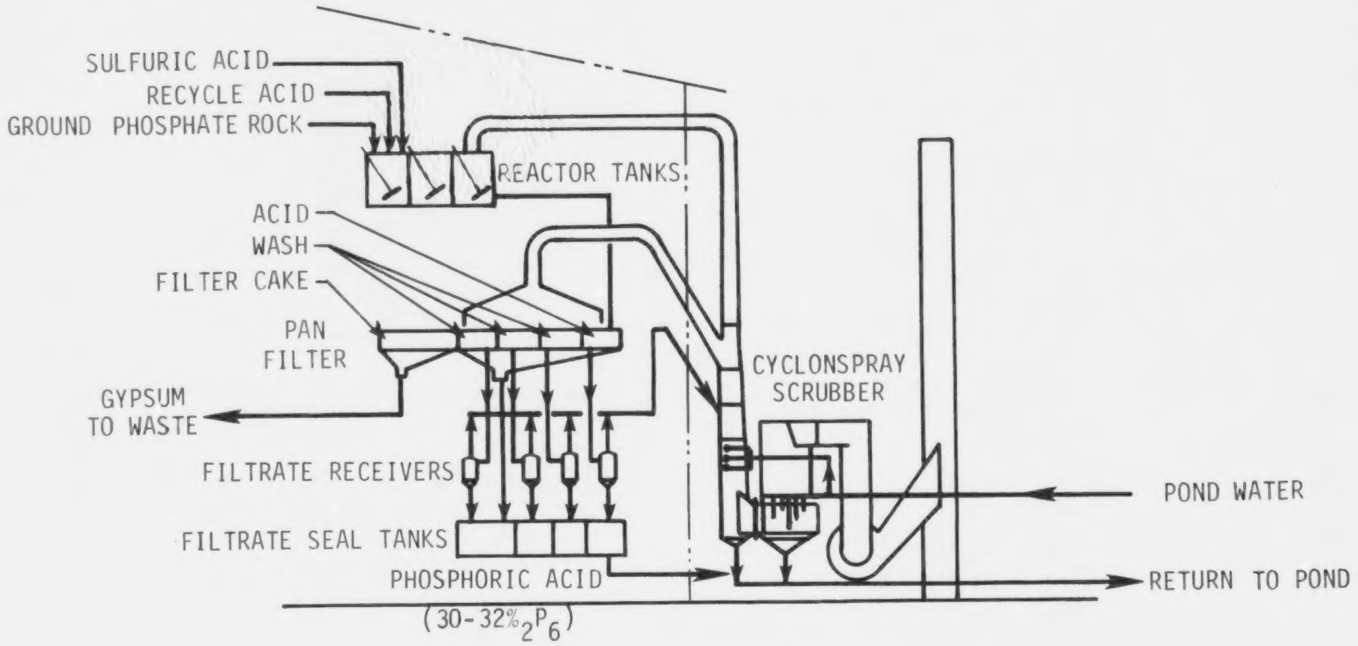

SULFURIC ACID
RECYCLE ACID
GROUND PHOSPHATE ROCK
REACTOR TANKS
ACID
WASH
FILTER CAKE
PAN FILTER
GYPSUM TO WASTE
FILTRATE RECEIVERS
FILTRATE SEAL TANKS
PHOSPHORIC ACID
(30-32%$_2$P$_6$)
CYCLONSPRAY SCRUBBER
POND WATER
RETURN TO POND

Figure 8-4: Wet Process Phosphoric Acid Flow Sheet (3)

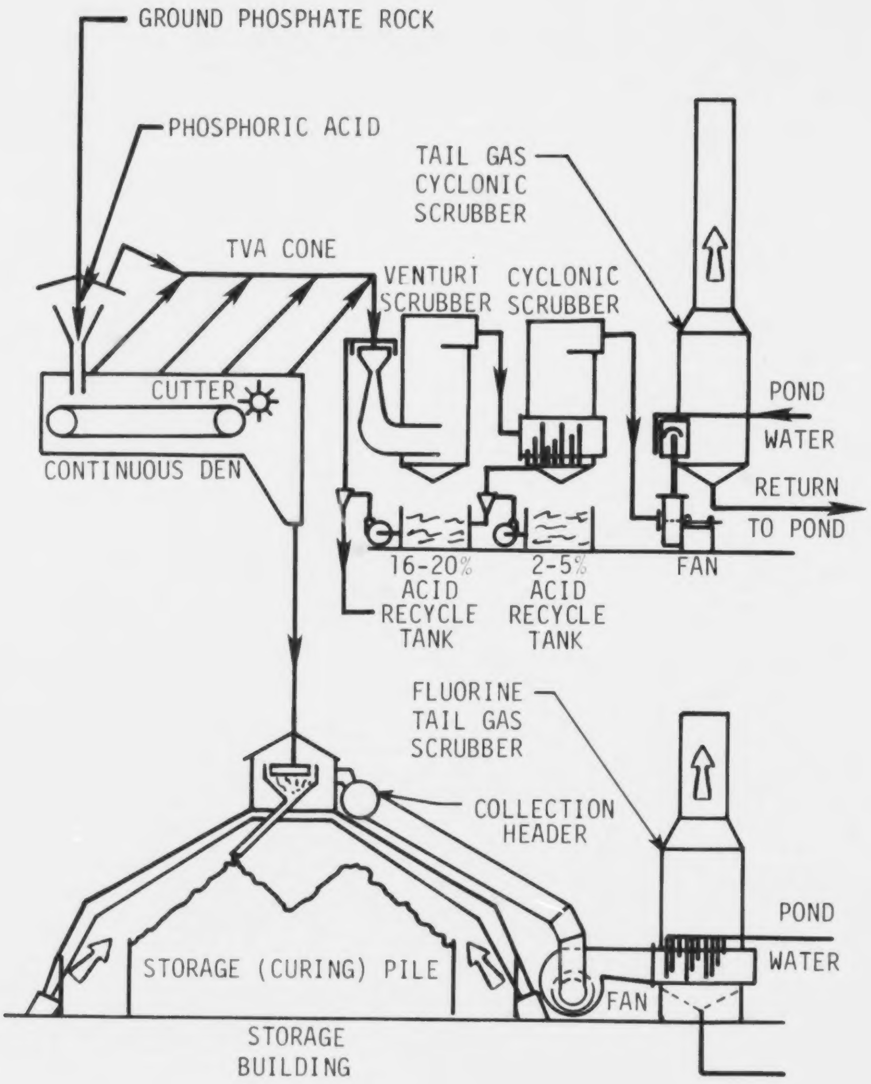
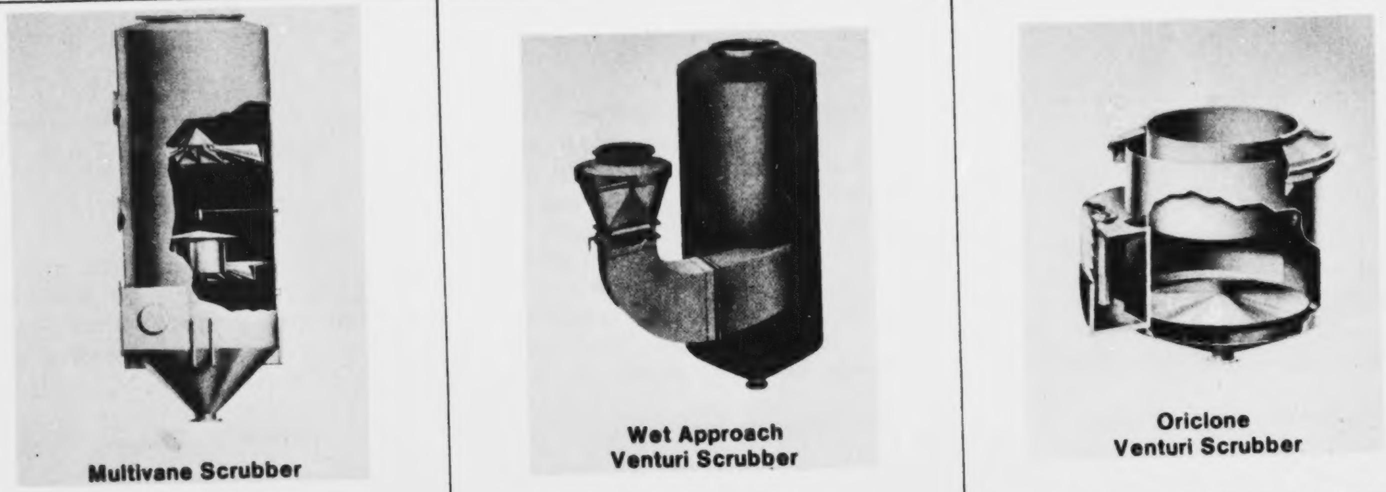

GROUND PHOSPHATE ROCK
PHOSPHORIC ACID
TAIL GAS CYCLONIC SCRUBBER
TVA CONE
VENTURI SCRUBBER
CYCLONIC SCRUBBER
CUTTER
CONTINUOUS DEN
POND WATER
RETURN TO POND
FAN
16-20% ACID RECYCLE TANK
2-5% ACID RECYCLE TANK
FLUORINE TAIL GAS SCRUBBER
COLLECTION HEADER
POND WATER
STORAGE (CURING) PILE
FAN
STORAGE BUILDING

Figure 8-5: ROP Triple Superphosphate Flow Sheet (3)



Multivane Scrubber

The Multivane Centrifugal Scrubber is particularly suited for applications involving heavy dust loads. This unit operates with centrifugal action between gas stream and liquid.

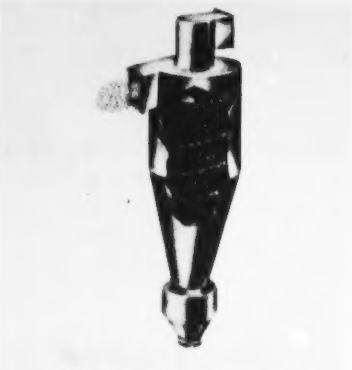
Wet Approach Venturi Scrubber

This high energy scrubber features a wetted wall inlet which eliminates wet-dry line build-up and permits direct recycle of high-solids liquid.

Oriclone Venturi Scrubber

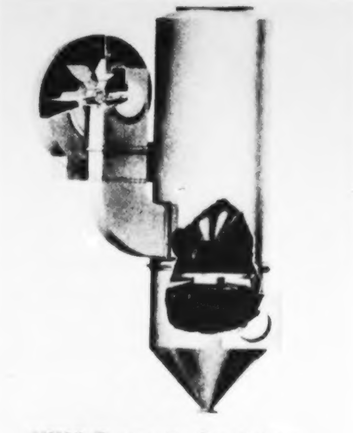
This high energy Venturi Scrubber provides ultra-efficient dust and fume control with 99+% efficiency into the sub-micron range. It combines venturi agglomeration and seperation.

Figure 8-6: Cyclonic and Wet Scrubbers Manufactured by Ducon (4)



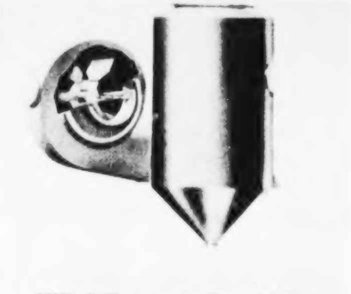
Duclone-Cyclones

Duclone Cyclones are designed for high efficiency and low resistance to assure maximum recovery of industrial dusts at minimum expense.



UW4-Dynamic Scrubber

This scrubber features three-way scrubbing action and incorporates a wet fan as an integral part of the unit. Dynamic scrubbing action offers 99+% cleaning efficiency in the 1-2 micron range, with low water requirements and low pressure drop.



UW-3 Dynamic Scrubber

This compact, unitized scrubber with self-cleaning wet fan features high dust collection efficiency in minimum space with low water requirements.

Figure 8-6: Cyclonic and Wet Scrubbers Manufactured by Ducon (4)
(continued)

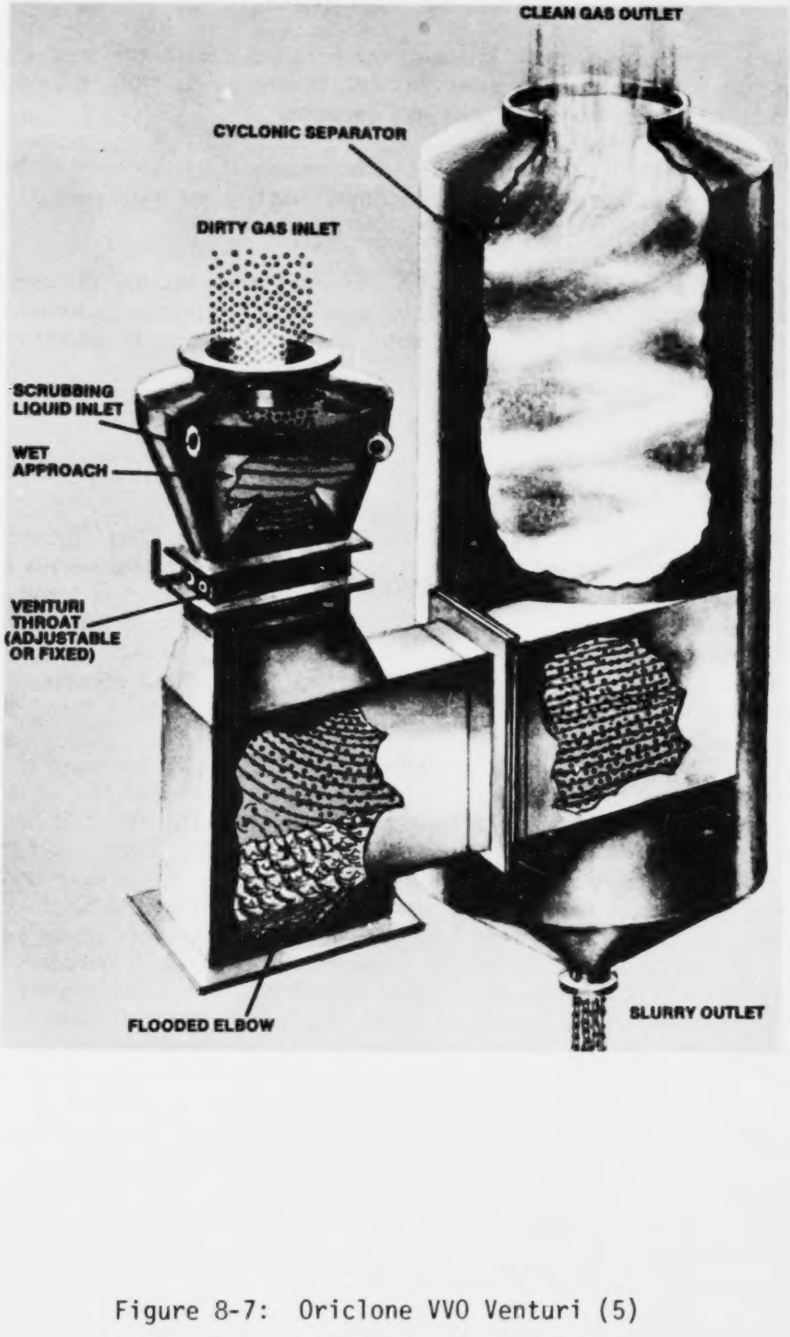

CLEAN GAS OUTLET
CYCLONIC SEPARATOR
DIRTY GAS INLET
SCRUBBING LIQUID INLET
WET APPROACH
VENTURI THROAT (ADJUSTABLE OR FIXED)
FLOODED ELBOW
SLURRY OUTLET

Figure 8-7: Oriclone VVO Venturi (5)

3. Low water requirements--In applications where liquid is recycled, the recycle tank can be made as an integral part of the entrainment separator. A fraction of the circulation load can be drawn off to a thickener or centrifuge for clarification and the remaining liquid returned to the scrubber. Scrubbing liquid lost in separation and through evaporation is made up by direct addition to the recycle tank.

4. Handles high temperature gases--VVO Scrubbers with the wet approach design feature can handle inlet gas temperatures to 1000 °F and higher without the requirement of separate quenchers.

5. Special construction for unusual environments--Scrubbers can be constructed of stainless steel, special alloys, plastics, or with special linings for severe corrosive conditions.

Figure 8-8 shows a schematic of the DAP process emphasizing Ducon's emission control (5). Since cyclones are normally considered process equipment, the emission control consists of individual Venturi scrubbers on four sources and a common tail gas scrubber.

8.3 The Ceilcote Company, Berea, Ohio

Since 1975 Ceilcote has been a unit of General Signals. Its Air Pollution Control Division has a line of wet scrubbers. The material of construction is usually FRP and thermoplastics. Tellerette tower packing is also manufactured and can be sold separately or as a packing in the scrubbing equipment. One of the company's most important developments has been the IWS scrubber which will be discussed. Ceilcote also provides conventional crossflow, Venturi and packed scrubbers which can be applied in the phosphate fertilizer industry.

The IWS ("Ionizing Wet Scrubber") is a new type of air pollution control device which collects aerosols and gaseous pollutants. The device combines the advantages of electrostatic precipitators and wet scrubbers within one unit to achieve a high rate of efficiency, while consuming a low amount of energy (6). Figure 8-9 shows a simplified cross-section and side view of the IWS scrubber (6). According to vendor literature, there is no defined lower size limit to aerosol collection, so that virtually the same collection efficiency is achieved on the very small aerosols (down to 0.025 microns) as it is on the large aerosols. As described in Section 5, aerosols of 2-5 microns and larger are collected through inertial impaction. Aerosols smaller than 3 microns become attracted and attached to collecting bodies through impaction and image force attraction. Image force attraction is a phenomenon in which the charged aerosols come close to the neutral surface (Tellerette packing/liquid droplets), induce a charge of opposite polarity, and are ultimately attracted to these surfaces. Collected particles are washed from the scrubber by the scrubber liquid. The vendor lists the following features for the IWS scrubber (6):

1. Collects most any type of micron/submicron particulate with equal efficiency.

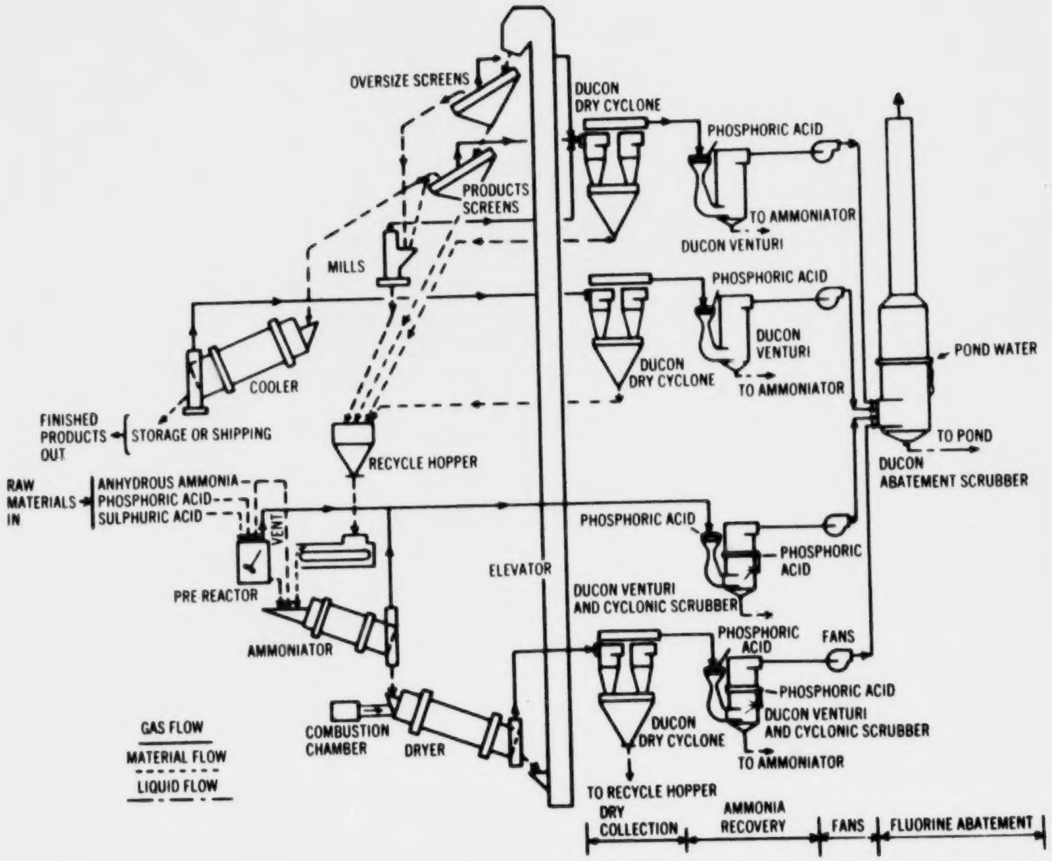

OVERSIZE SCREENS
PRODUCTS SCREENS
MILLS
COOLER
FINISHED PRODUCTS OUT
STORAGE OR SHIPPING
RAW MATERIALS IN
ANHYDROUS AMMONIA
PHOSPHORIC ACID
SULPHURIC ACID
VENT
PRE REACTOR
AMMONIATOR
RECYCLE HOPPER
COMBUSTION CHAMBER
DRYER
ELEVATOR
GAS FLOW
MATERIAL FLOW
LIQUID FLOW
DUCON DRY CYCLONE
PHOSPHORIC ACID
TO AMMONIATOR
DUCON VENTURI
PHOSPHORIC ACID
DUCON VENTURI
DUCON DRY CYCLONE
TO AMMONIATOR
POND WATER
TO POND
DUCON ABATEMENT SCRUBBER
PHOSPHORIC ACID
PHOSPHORIC ACID
DUCON VENTURI AND CYCLONIC SCRUBBER
PHOSPHORIC ACID
FANS
PHOSPHORIC ACID
DUCON VENTURI AND CYCLONIC SCRUBBER
DUCON DRY CYCLONE
TO AMMONIATOR
TO RECYCLE HOPPER
DRY COLLECTION
AMMONIA RECOVERY
FANS
FLUORINE ABATEMENT

Figure 8-8: DAP Process Schematic Including Ducon Scrubbers (5)

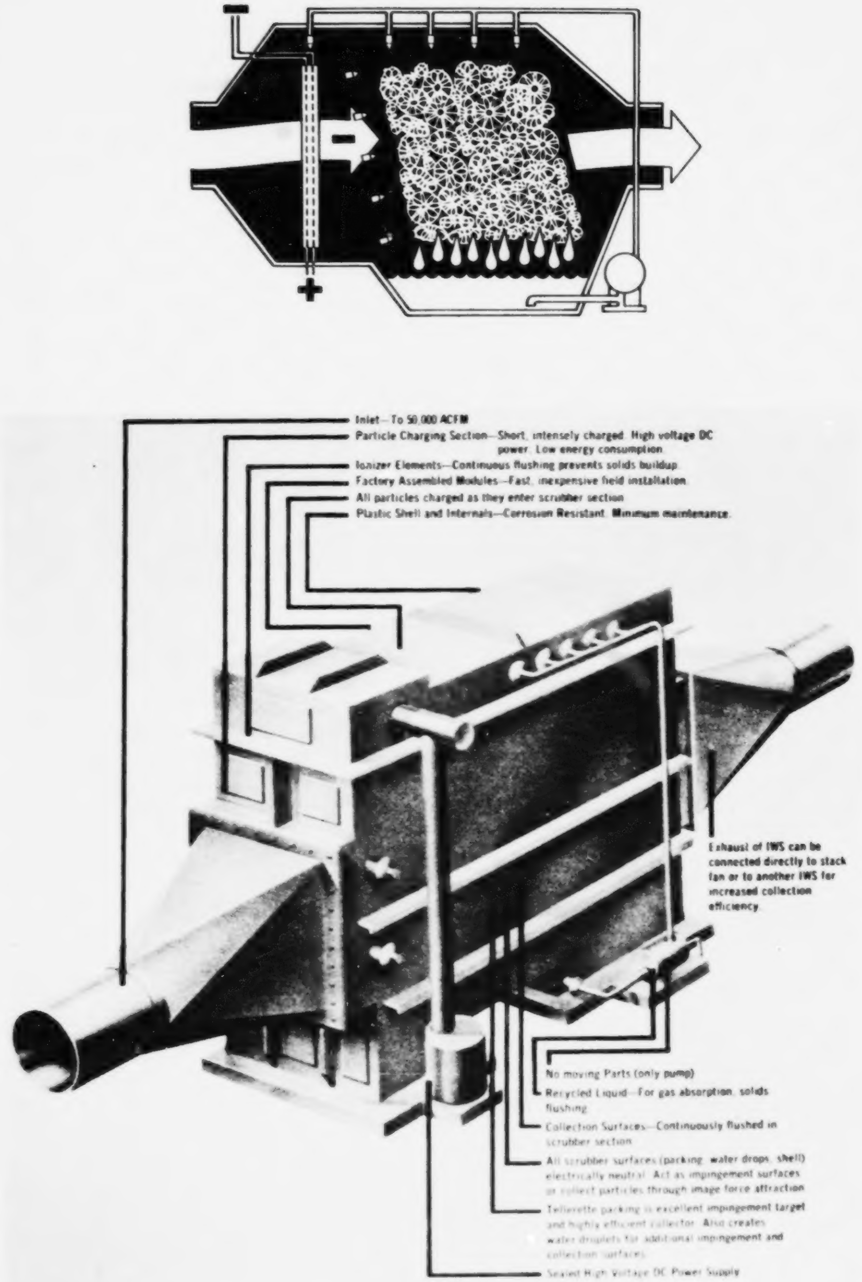

Inlet—To 50,000 ACFM
Particle Charging Section—Short, intensely charged. High voltage DC power. Low energy consumption.
Ionizer Elements—Continuous flushing prevents solids buildup.
Factory Assembled Modules—Fast, inexpensive field installation.
All particles charged as they enter scrubber section.
Plastic Shell and Internals—Corrosion Resistant. Minimum maintenance.
Exhaust of IWS can be connected directly to stack fan or to another IWS for increased collection efficiency.
No moving Parts (only pump)
Recycled Liquid—For gas absorption, solids flushing.
Collection Surfaces—Continuously flushed in scrubber section.
All scrubber surfaces (packing, water drops, shell) electrically neutral. Act as impingement surfaces or collect particles through image force attraction.
Tellerette packing is excellent impingement target and highly efficient collector. Also creates water droplets for additional impingement and collection surfaces.
Sealed High Voltage DC Power Supply

Figure 8-9: Simplified Cross-Section and Side-View of the IWS Scrubber (6)

2. Removes solid and liquid particulates and noxious gases simultaneously.
3. Acts as a fractional collector. Percent of particles removed varies little with load.
4. Collection efficiency remains constant with turndown from 100% to 0% load.
5. Consumes little energy (2.0 to 2.5 BHP per 1000 CFM per stage).
6. Operates at low static pressure drops (less than 2.0 inches W.G. per stage).
7. Is impervious to corrosive atmospheres because of predominance of plastic construction.
8. Provides long operating life and requires little maintenance.
9. Modular construction simplifies on-site erection.
10. Handles large variations in process flows without decreased efficiency.
11. Can be continually upgraded by adding on additional modules as requirements change.

McIlvaine lists the following advantages and disadvantages for the IWS Scrubber (1).:

> DESIGN ADVANTAGES: Unit will not only remove coarse particles, but will remove fine particles at high efficiency and low energy consumption (e.g., fine particles 0.02 - 2 microns are removed nearly as efficiently as >2 micron particles and energy required is approximately equal to a Venturi scrubber Δ P of 10 inches water gauge). Collection efficiency remains nearly constant with turn down from 100% to 0% load. The fiberglass reinforced polyester material of construction provides a lightweight, corrosion-resistant scrubber. Factory assembled modules up to 50,000 CFM reduce installation costs.
>
> DESIGN DISADVANTAGES: High voltage-liquid combinations necessitate strict safety precautions and maintenance and operating procedures. Plastic materials of construction must be protected from high temperature gases. Clean scrubbing liquor must be used so a clarifier is required. Installation space requirements for the system could be greater than for a similar conventional modular wet scrubber because of the auxiliary electrical requirements.

Since this unit is relatively new, it has not been widely applied in the phosphate fertilizer field. It has a good potential in DAP emission control where new evidence (7) shows that fluorides are emitted in the form of submicron aerosols (mostly ammonium bifluorides).

8.4 Heil Process Equipment Company, Avon, Ohio

Heil, a Division of Dart Industries, Inc., has 40 years of experience in corrosion-resistant control equipment. It has a number of fume scrubber installations in the phosphate fertilizer industry. The majority of applications involve removal of dust combined with acidic gases and ammonia. Fume scrubbers have also been used for scrubbing and in some cases recovery of hydrofluoric and fluosilic acid from acidulation operations.

Figure 8-10 shows three arrangements of Heil 720 Venturi scrubbers. Although these units of conventional design represent a small market share of the total Venturi market, their share in FRP is significant. Heil also has a significant market share in water jet eductor-Venturi scrubbers (9). Applications in the phosphate fertilizer industry involve recovery and scrubbing of hydrofluoric and fluosilic acid.

The design advantages include compact size and elimination of the fan, while the disadvantages consist of a high water requirement and a need for high pressure pumps (1).

8.5 Major Engineering Firms Designing Phosphate Fertilizer Plants

There are a number of engineering firms involved in the design of phosphate fertilizer plants. The following three appear to be the leading ones:

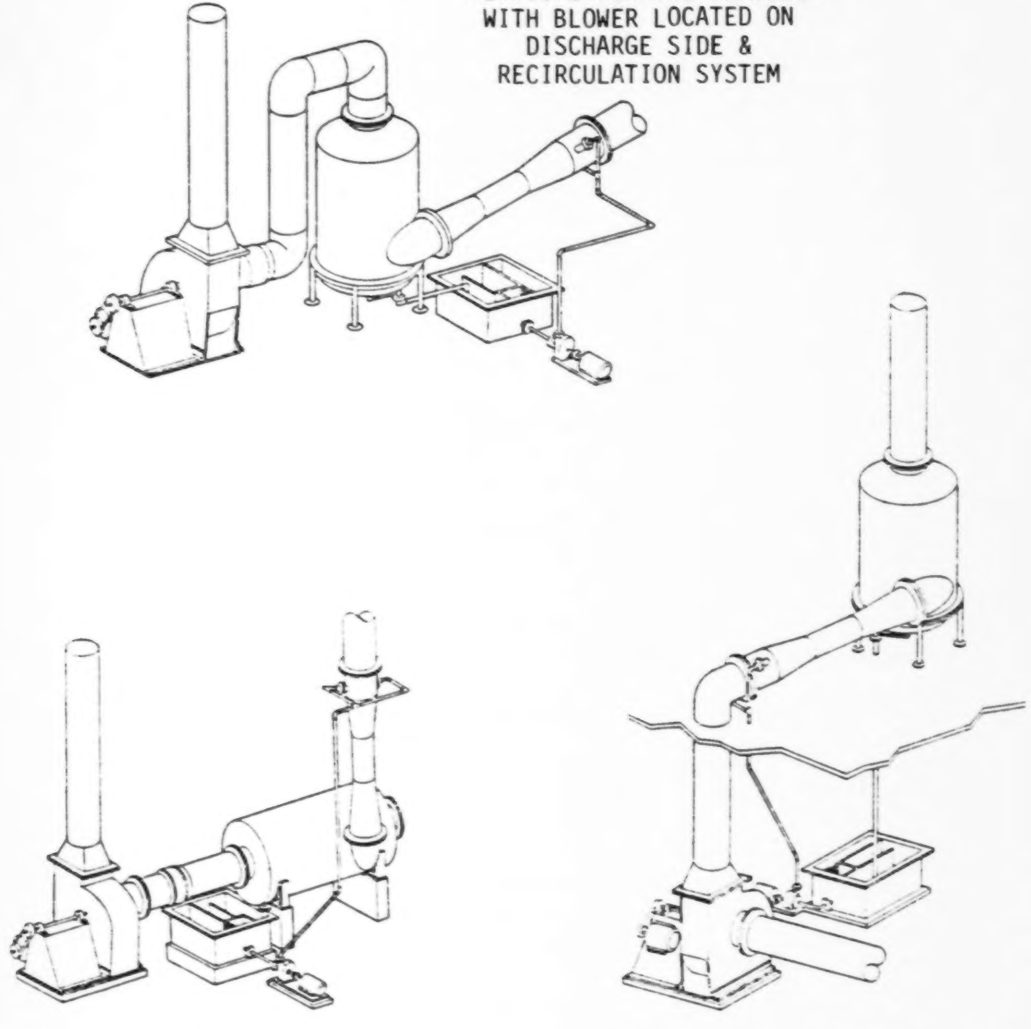
1. Davy Powergas (including Wellman-Lord technology)
2. Jacobs Engineers (including Dorr-Oliver technology)
3. Waverly

Davy Powergas has designed and constructed the largest number of phosphate fertilizer plants in North America. According to the Davy Powergas brochure, contracts for 38 out of the last 43 WPPA plants and 31 out of the last 34 GTSP-DAP plants were awarded to Davy Powergas (10). Consequently, only Davy Powergas will be briefly described as representative of engineer-constructor firms dealing with the Phosphate Fertilizer Industry. It is also important to mention that Davy Powergas designs its own air pollution control equipment for the industry.

The wet process phosphoric acid plants designed by Davy Powergas are based on the Prayon process. Figure 8-11 shows a typical WPPA process flowsheet (11). Since this process is similar to one described in Section 4, it will not be described here. According to Davy, the economic advantages of the Prayon process are (10):

1. Overall reliability and onstream factor is greater than 90% which is superior to other processes, making the Prayon Process the industry standard in North America.

2. Very adaptable to the use of any type of rock. Prayon has the expertise in testing all grades of rock to enable optimum design.



VERTICAL VENTURI SCRUBBER
WITH BLOWER LOCATED ON
DISCHARGE SIDE &
RECIRCULATION SYSTEM

HORIZONTAL VENTURI SCRUBBER
WITH BLOWER LOCATED ON
DISCHARGE SIDE WITH TYPICAL
RECIRCULATION TANK, PUMP,
AND PIPING.

VERTICAL VENTURI SCRUBBER
WITH BLOWER LOCATED ON
INLET SIDE INCLUDING
RECIRCULATION SYSTEM

Figure 8-10: Three Arrangements of Heil 720 Venturi Scrubbers (8)

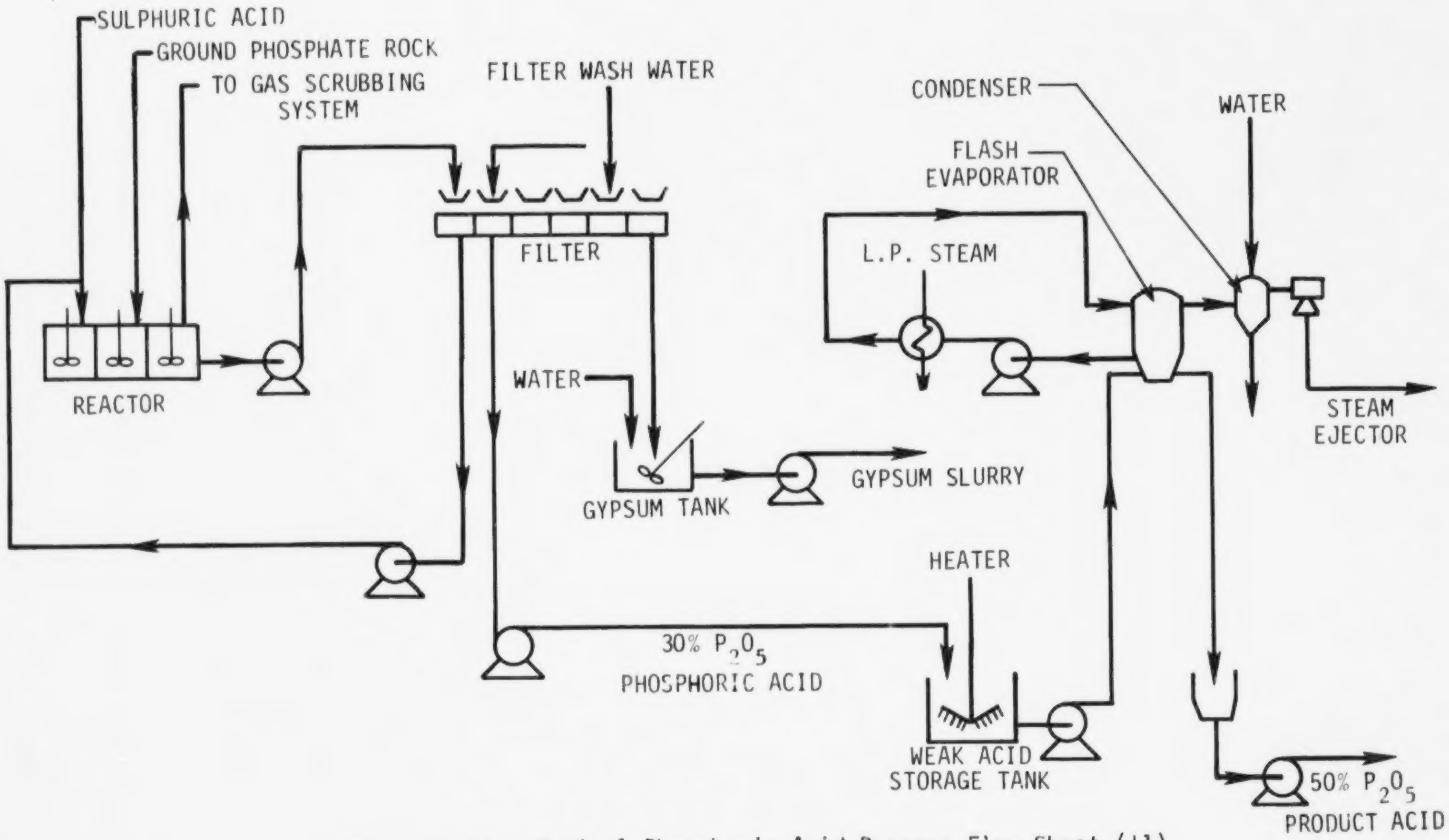

SULPHURIC ACID
GROUND PHOSPHATE ROCK
TO GAS SCRUBBING SYSTEM
FILTER WASH WATER
REACTOR
FILTER
WATER
GYPSUM TANK
GYPSUM SLURRY
30% P_2O_5 PHOSPHORIC ACID
HEATER
WEAK ACID STORAGE TANK
CONDENSER
FLASH EVAPORATOR
L.P. STEAM
WATER
STEAM EJECTOR
50% P_2O_5 PRODUCT ACID

Figure 8-11: Typical Phosphoric Acid Process Flow Sheet (11)

3. Plant design and layout minimizes maintenance costs, less than 5% of capital per year.

4. Defoamer usage is much less than competing processes, less than 25¢/ton P_2O_5 as compared to \$1 to \$2.00/ton P_2O_5 for others.

5. The adaptability of the Prayon Process is very suitable for the construction of large plants, (e.g., International Minerals & Chemical Corp., 2 trains @ 912 TPD and Agrico, one train @ 1200 TPD).

In designing granulation plants Davy uses DPG and Fisons technology. Figure 8-12 shows a granulation plant process flowsheet (11). This flowsheet is typical for a range of nitrogen-phosphorus and nitrogen-potassium-phosphorus granulated fertilizers. Typically, these plants are used for manufacture of GTSP and DAP; however, depending on the solid raw materials available--powder MAP, ground phosphate rock, ground TSP, potassium chloride, etc.--a range of NPK fertilizers can be manufactured in a similar way. The advantages of the Davy Powergas design of the granulation plants are (10):

1. Overall reliability and onstream factor is greater than 90%.

2. The use of the Slurry Process and Rotary Granulator lowers capital cost installation as compared to Pug Mills.

3. Plant design and layout minimizes maintenance costs, 5% or less of capital per year.

Davy Powergas designs its own air pollution control equipment but no information on design specifics is available. In the past Davy Powergas also worked closely with Teller Environmental System on the design of emission controls, specifically the crossflow scrubber. Figure 8-13 shows Teller's design of a crossflow packed scrubber which was applied on various phosphate fertilizer processes and, together with similar designs, represents best available control technology. This scrubber permits high gas and liquid flowrates, is modular in design and has a maximum capability for particulate feed or deposition (12). As reported by EPA, the emissions for a well designed Teller Scrubber range from 1-3 PPM of fluorides, essentially in equilibrium with the pond water in the order of 0.003 to 0.01 lb F/ton P_2O_5 (12).

8.6 References

1. McIlvaine Scrubber Manual, The McIlvaine Company, Northbrook, Illinois.

2. Environmental Elements Corporation, ENELCO Scrubbers, Form DVGM, Rev. 10/76.

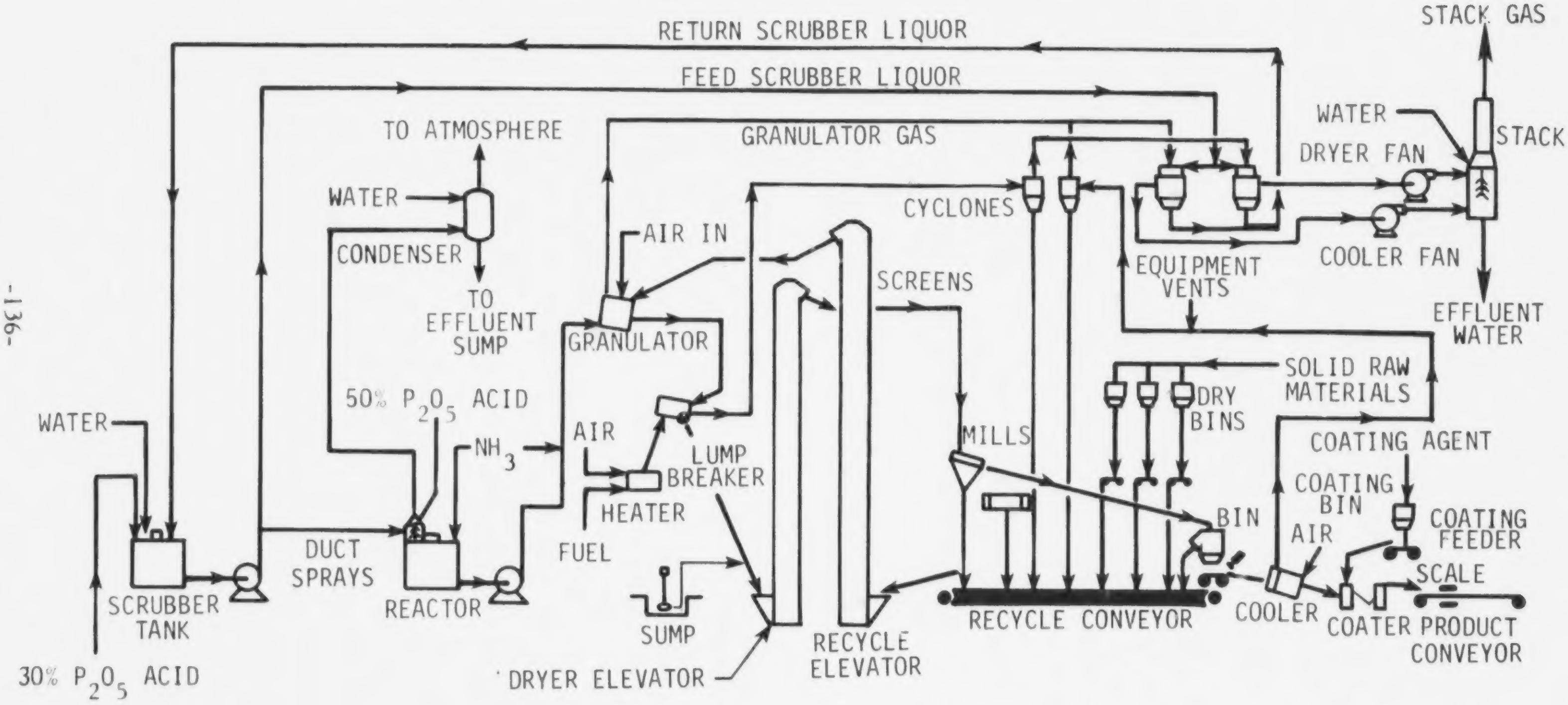

RETURN SCRUBBER LIQUOR
FEED SCRUBBER LIQUOR
STACK GAS
WATER
STACK
TO ATMOSPHERE
GRANULATOR GAS
DRYER FAN
WATER
CONDENSER
CYCLONES
AIR IN
COOLER FAN
EQUIPMENT VENTS
SCREENS
TO EFFLUENT SUMP
GRANULATOR
EFFLUENT WATER
SOLID RAW MATERIALS
50% P_2O_5 ACID
DRY BINS
WATER
NH_3
AIR
MILLS
COATING AGENT
LUMP BREAKER
HEATER
COATING BIN
DUCT SPRAYS
BIN
AIR
COATING FEEDER
FUEL
SCALE
SCRUBBER TANK
REACTOR
SUMP
RECYCLE CONVEYOR
COOLER
COATER
PRODUCT CONVEYOR
RECYCLE ELEVATOR
30% P_2O_5 ACID
DRYER ELEVATOR

Figure 8-12: Granulation Plant Process Flow Sheet (11)

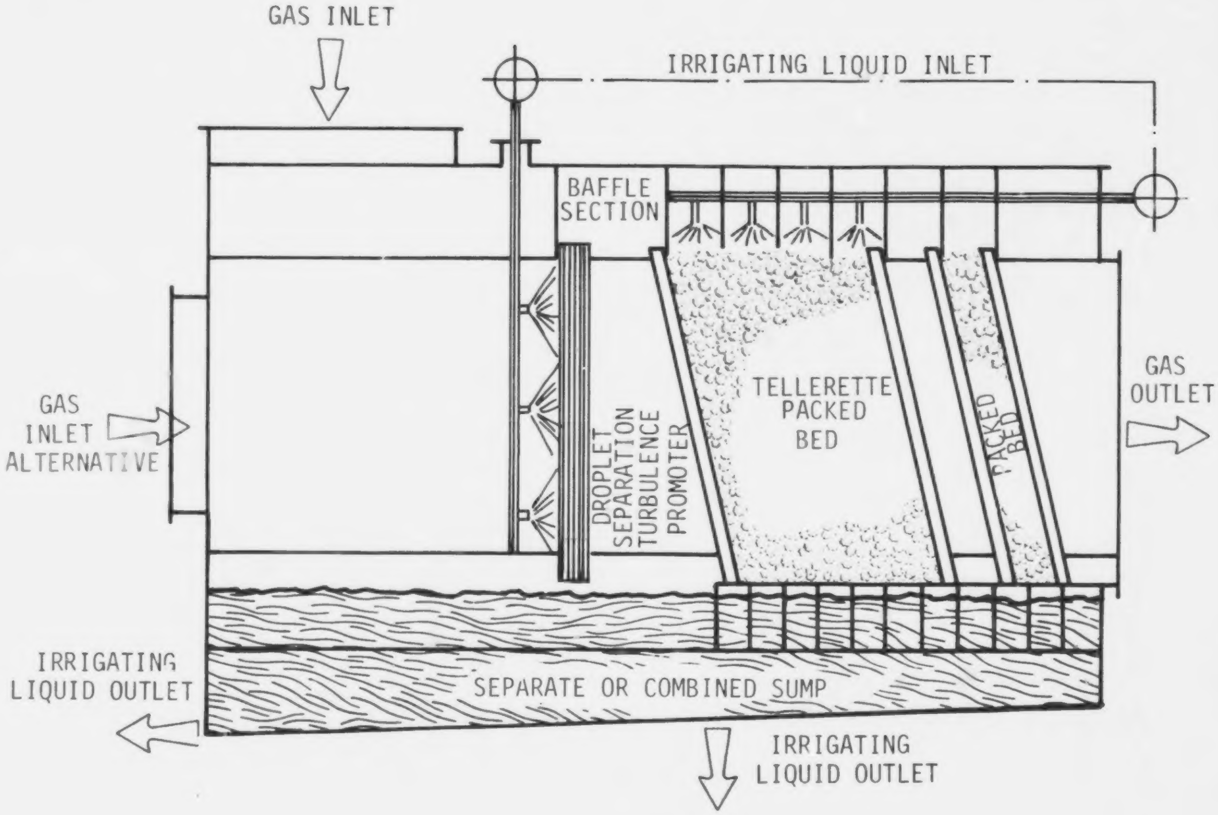

GAS INLET
IRRIGATING LIQUID INLET
BAFFLE SECTION
GAS INLET ALTERNATIVE
DROPLET SEPARATION TURBULENCE PROMOTER
TELLERETTE PACKED BED
PACKED BED
GAS OUTLET
IRRIGATING LIQUID OUTLET
SEPARATE OR COMBINED SUMP
IRRIGATING LIQUID OUTLET

Figure 8-13: Teller Crossflow Scrubber (12)

3. Hill, L.J., Install Adequate System at Start to Control Fertilizer Emission, Croplife, March 1976.

4. Ducon Bulletin No. W 7572, Dynamic Gas Scrubber Type UW-4.

5. Ducon Bulletin No. W 9075, Ducon Venturi Scrubber Type VVO.

6. Ceilcote Bulletin 1201, Guide to Selection of Air Pollution Control Equipment.

7. Private Communication with Dr. A. Teller.

8. Heil Bulletin No. B-720-2, Heil Venturi Scrubbers.

9. Heil Bulletin No. B-770-1, Water Jet Eductor Venturi Scrubbers.

10. Davy Powergas, Qualification Summary for Phosphate Chemicals.

11. Davy Powergas, Bulleting D-20, Phosphate Fertilizer Plants.

12. Teller, A.J., Scrubbers in the Fertilizer Industry, Their Success, Near Future and Eventual Replacement, presented at the Fertilizer Round Table, Washington, D.C., November 1973, 8 pp.

9.0 RECOMMENDED RD&D PROJECTS

One of the major objectives of this project was to identify gaps in information and determine needs for future research and development and full scale demonstration. This section will recommend RD&D programs needed for a better understanding of the phosphate fertilizer industry's environmental problems and available solutions. The discussion of proposed RD&D programs outlines background information and generalized methodology as to how such programs can be carried out. It was beyond the scope of this work to prepare detailed descriptions of specific RD&D programs. A detailed scope of work for such projects can be prepared after the decision is made as to which studies to pursue.

The following recommended RD&D projects are described in this section:

1. An epidemiological study of the phosphate fertilizer industry
2. Studies of gypsum pond emissions and chemistry
3. An evaluation and optimization of wet scrubbers
4. An ammonia-sulfuric acid mist interaction atmospheric chemistry and dispersion modeling study
5. A demonstration of a dry system for fluoride removal
6. An evaluation of the Kimre mist eliminator.

9.1 Epidemiological Study of the Phosphate Fertilizer Industry

9.1.1 Background

The phosphate fertilizer industry spends a considerable amount of money for the purchase, installation and operation of pollution control equipment. Some industry spokesmen consider that industry has gone as far as necessary in emission control and that stricter control is warranted only if a health hazard is demonstrated. There is increasing concern that environmental pollution plays an important role in the development of cancer, even though the etiology of most cancers is unknown. The relationship of environmental agents to the carcinogenic risk to man has been discussed by the International Agency for Research on Cancer (1):

> Evaluation of the carcinogenic risk to man of suspected environmental agents rests on purely observational studies. Such studies must cover a sufficient variation in levels of human exposure to allow a meaningful relationship between cancer incidence and exposure to a given chemical to be established. Difficulties arise in isolating the effects of individual agents, however, since people are usually exposed to multiple carcinogens.

The initial suggestion of a relationship between an agent and disease often comes from case reports of patients with similar exposures. Variations and time trends in regional or national cancer incidences, or their correlation with regional or national 'exposure' levels, may also provide valuable insights. Such observations by themselves cannot, however, in most circumstances be regarded as conclusive evidence of carcinogenicity.

In the case of the phosphate fertilizer industry, the major concern would be low level radioactivity from Uranium in phosphate rock, gypsum ponds, and stacks. Natural uranium contains approximately 99.82% uranium 238 and 0.71% uranium 235. The decay chain of uranium 238 (known as the uranium-radium family), shown in Figure 9-1, is of primary importance (2). The isotopes formed from uranium 238 present varying degrees of hazard. From the standpoint of water pollution, the radioisotope radium 226 is the most hazardous. It has a maximum permissible concentration (MPC) an order of magnitude less than any of the other decay isotopes. Phosphate rock contains approximately 50 microcuries of radium per metric ton (2).

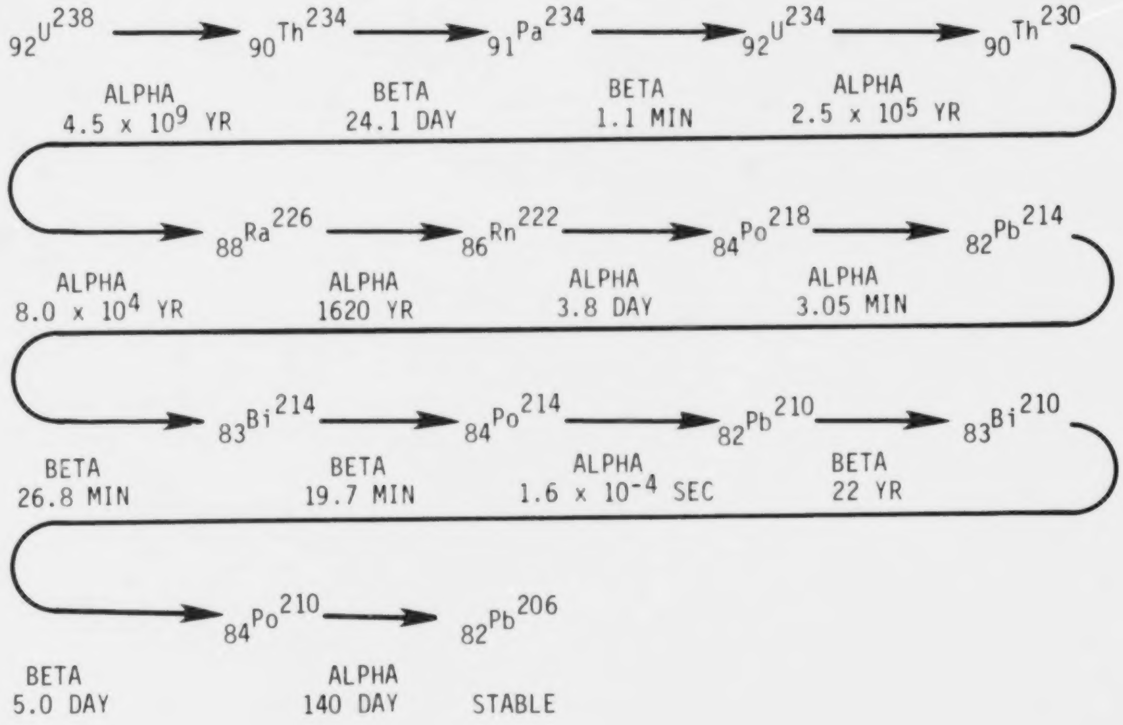
Radium tends to replace calcium in bone. Persons working in industry may have been exposed for a number of years to low radiation. The methodology of studying the health effects of workers in industry have been well defined and applied to specific problems (3,4).

Of equal concern is the possibility that effluents from industrial waste may lead to adverse health effects in persons living in areas near the plants.
While the doses of exposure to such general populations are undoubtedly less than those for workers, such exposures impact on a larger population for longer periods of time. Any effects seen are likely to be of a lower magnitude and thus are more difficult to detect.

In the United States, 83% of the phosphate mining in 1968 was done in Florida and North Carolina with the bulk done in Florida. In Florida the industry is concentrated in Polk and Hillsborough counties. Figure 9-2 shows the epidemiological data for specific cancers for white males in the State of Florida. Table 9-1 ranks the counties in Florida based on the cancer mortality rate from respiratory tract cancers. Although these data may appear to indicate that there is no problem regarding respiratory types of cancer in Polk County especially, the conclusive evidence of carcinogenicity can be derived only through a careful epidemiological study. The following generalized methodology, with special emphasis on bone cancer, is recommended.

9.1.2 Generalized Methodology for Epidemiological Study

In collecting information on human populations to assess the health effects of pollution, either mortality data (the proportion of deaths to population) or morbidity data (relative incidence of disease) may be assembled. Since many cancers lead eventually to death, the use of mortality data in assessing the occurrence of cancer is logical. Further, some mortality data are routinely collected by governmental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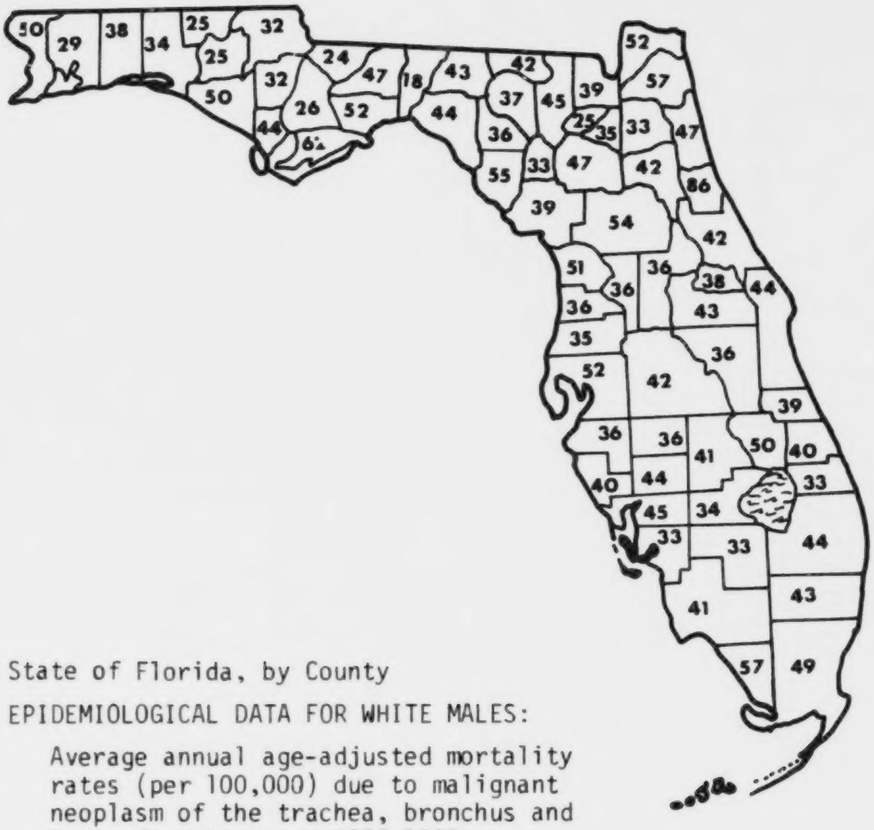
4.5×10^{9} YR
$_{90}Th^{234}$
BETA
24.1 DAY
$_{91}Pa^{234}$
BETA
1.1 MIN
$_{92}U^{234}$
ALPHA
2.5×10^{5} YR
$_{90}Th^{230}$
ALPHA
8.0×10^{4} YR
$_{88}Ra^{226}$
ALPHA
1620 YR
$_{86}Rn^{222}$
ALPHA
3.8 DAY
$_{84}Po^{218}$
ALPHA
3.05 MIN
$_{82}Pb^{214}$
BETA
26.8 MIN
$_{83}Bi^{214}$
BETA
19.7 MIN
$_{84}Po^{214}$
ALPHA
1.6×10^{-4} SEC
$_{82}Pb^{210}$
BETA
22 YR
$_{83}Bi^{210}$
BETA
5.0 DAY
$_{84}Po^{210}$
ALPHA
140 DAY
$_{82}Pb^{206}$
STABLE

Figure 9-1: Uranium-Radium Family Mode of Decay (2)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State of Florida, by County

EPIDEMIOLOGICAL DATA FOR WHITE MALES:

Average annual age-adjusted mortality rates (per 100,000) due to malignant neoplasm of the trachea, bronchus and lung, for the years 1950-1969.

Source: U. S. Dept. of Health, Education and Welfare (1974).

Average, U.S.A. = 37.98
Florida = 44.93

Figure 9-2: Epidemiological Data for White Males, State of Florida (5)

TABLE 9-1. CANCER MORTALITY RATE, STATE OF FLORIDA (5)

Rank	County	Cancer Mortality Rate Lung, Trachea, Bronchus	Rank	County	Cancer Mortality Rate Lung, Trachea, Bronchus
1	Flagler	85.8	35	Sarasota	40.0
2	Franklin	62.2	36	St. Lucie	39.8
3	Monroe	57.1	37	Baker	39.1
4	Duval	56.8	38	Indian River	38.9
5	Dixie	55.2	39	Levy	38.6
6	Marion	53.7	40	Seminole	38.4
7	Hillsborough	52.5	41	Okaloosa	37.7
8	Nassau	52.4	42	Suwanee	37.2
9	Wakulla	52.2	43	Hardee	36.3
10	Citrus	51.2	44	Lake	36.3
11	Okeechobee	50.1	45	Sumter	36.2
12	Escambia	50.0	46	Lafayette	36.1
13	Bay	49.7	47	Hernando	36.1
14	Dade	49.2	48	Manatee	36.0
15	Alachua	47.5	49	Osceola	35.8
16	St. Johns	47.4	50	Bradford	34.9
17	Leon	47.2	51	Pasco	34.6
18	Charlotte	45.0	52	Glades	34.2
19	Columbia	44.9	53	Walton	34.0
20	Palm Beach	44.2	54	Hendry	33.1
21	Gulf	44.1	55	Lee	33.1
22	Brevard	44.1	56	Clay	33.0
23	DeSoto	43.9	57	Martin	32.7
24	Taylor	43.7	58	Gilchrist	32.6
25	Pinellas	43.2	59	Jackson	32.5
26	Broward	43.0	60	Calhoun	32.5
27	Madison	42.8	61	Santa Rosa	28.8
28	Orange	42.6	62	Liberty	25.7
29	Putnam	42.5	63	Union	25.5
30	Hamilton	42.2	64	Holmes	24.8
31	Polk	41.8	65	Washington	24.6
32	Volusia	41.7	66	Gadsden	24.3
33	Highlands	41.2	67	Jefferson	18.6
34	Collier	41.0			

NOTES: 1) Average annual age-adjusted mortality rates (per 100,000) due to malignant neoplasm of the trachea, bronchus, and lung, for the years 1950-1969.

2) Source: U.S. Department of Health, Education and Welfare (1974).

agencies and thus may be assembled at relatively low cost. Many other diseases, such as cardiovascular disease and mental illness, may not lead to death; therefore, it is necessary to evaluate morbidity data.

In categorizing the methods to be used in assessing the possible effects on health of living in the area of a phosphate fertilizer plant, a primary question is whether data collected for other reasons may be used. A secondary question is whether the data are on mortality or on morbidity. Finally, data can be collected by following groups of exposed and non-exposed persons or by evaluating past exposures in groups of diseased and non-diseased persons. Not all of the possibilities are realistic, and only six strategies will be considered.

These strategies can be outlined as:

1. Evaluation of routinely collected data
    a. Mortality
    b. Morbidity
2. Evaluation of specifically collected data
    a. Mortality follow-up of exposed groups
    b. Mortality evaluation of decreased persons
    c. Morbidity ad hoc evaluation
    d. Morbidity case-control surveillance

A short description of the above six strategies follows.

1. Evaluation of Routinely Collected Data

a. Mortality

Mortality rates have been used to evaluate the associations of cancer with counties in which chemical (6) or petroleum (7) plants are located. A similar evaluation of counties with phosphate fertilizer plants should be carried out.

The methodology for such an evaluation is straightforward. The first step is to select counties in which there are phosphate fertilizer plants, complete the cancer-specific mortality rates for the entire set of such counties, and compare these rates to those of the entire U.S. population. If higher rates of specific cancers are found in counties where these plants are located, the possibility that the cancer is a result of the industry's presence must be considered.

Such evidence, however, is extremely tenuous. There may be other characteristics of the general population in those counties which are associated with the specific cancer(s). For this reason, a second step should be performed to evaluate this possibility. Control counties, similar to the "exposed" counties, should be selected, and the cancer experience in these counties should be evaluated.

b. Morbidity

Morbidity data are routinely collected by the National Health Survey. However, these data are based on a relatively small sample and are unlikely to provide specific data on areas in which phosphate fertilizer plants are located.

Morbidity data are also collected by the Professional Activities Service (PAS) of the Commission on Professional Activities (CPHA). Roughly 40% of the hospitals in the United States provide diagnostic information to the PAS. As an example of the manner in which morbidity data can be used in an epidemiological study, data from the PAS have been used as the starting point for an evaluation of the relationship between estrogen usage and myocardial infarction (8).

It is possible that the PAS serves many hospitals in counties where the phosphate fertilizer industry is located. Such counties could be selected and compared to control counties in the distribution of diagnoses reported to the PAS.

2. Evaluation of Specially Collected Data

a. Mortality Follow-Up of Exposed Groups

If persons live for many years in the environs of a phosphate fertilizer plant, and if effluent from the plant affects their health, it is possible that such an effect may be detectable from the pattern of cause of death among these people. Through the use of census records or other population lists extending back many years, an "exposed" population is assembled. A control population can be also assembled from the same records. The methodology of such a study is uncomplicated but the approach may be too insensitive to detect small casual associations.

b. Mortality Evaluation of Deceased Persons

Rather than using mass data collected on populations, the cause of death can be evaluated by examining individual death certificates. For counties where the phosphate fertilizer industry is located, and for control counties, all death certificates for a number of years can be assembled. Two basic comparisons would be from such data: between counties and within counties.

c. Morbidity Ad Hoc Evaluation

Specially-collected morbidity data would be based on patient records from hospitals in the phosphate fertilizer industry area. Rather than reviewing all records, only specific diseases linked to this industry exposure would be reviewed.

d. Morbidity Case-Control Surveillance

Hospitals serving populations where phosphate fertilizer plants are located could be monitored. Patients could be interviewed, both about their occupational exposure to the fertilizer industry and about their residence pattern. Analysis would include the relationship between specific illness and residence near the plant.

The various types of studies outlined are discussed only in general terms. Each of the studies discussed would seem to be feasible. The studies in which existing data are utilized could be done in one or two years. The studies in which data is to be collected would require three to five years at least. Even larger programs may be needed if patterns of change with time are to be evaluated.

Whether an association in general populations between disease and industrial pollution can be found is problematic. Data on human populations are subject to much variation and weak associations may not be detectable. If such associations are to be found, relatively large amounts of data must be collected and fairly extensive analysis must be done. Associations seen must be duplicated in independent populations. Interpretation of any association must be conservative.

The most cost-effective way to proceed with an epidemiological study for the phosphate fertilizer industry appears to be a pilot study. The main targets would be the plants with gypsum ponds near populated areas. Only a dozen plants would fall in this category. As a first cut, the mortality rates for the counties where these plants are located should be compared with rates for the entire U.S. population. Simultaneously, control counties which have phosphate fertilizer plants that do not have gypsum ponds should be selected and rates examined. The comparison of these mortality rates can serve as a preliminary indication of risk associated with the phosphate fertilizer plants. If the pilot study shows significant association, a follow-up study to explain its causes should be planned. A more comprehensive epidemiological study of the complete phosphate fertilizer industry does not appear to be justified in the light of relatively high cost and possible inconclusive results. The costs and time for a pilot epidemiological study vary greatly depending on the availability of information.

9.2 Studies of Gypsum Pond Emissions and Chemistry

One concern about wet scrubbing for air emission control has been that this technique in most cases does not result in the ultimate disposal of pollutants. Frequently air pollution is simply replaced by water pollution or a solid waste management problem. This concern fully applies to fluoride scrubbing in the phosphate fertilizer industry. The fluorides are removed from stationary sources with a high efficiency (as a rule over 95%) and they are then transferred to a gypsum pond where most of them become fixated. The remaining portion may be released to the atmosphere. These emissions are governed by liquid/gas equilibria which have not been thoroughly investigated. Table 4-2 indeed indicates that emissions of fluorides from gypsum ponds by far surpass the emissions from other sources in a WPPA plant.

Section 6 discussed at length all alternatives for gypsum pond emission control, but no economical means of control surfaced.

9.2.1 Study of Fluorine Distribution

Section 6-2 discussed gypsum pond chemistry with special emphasis on fixation of fluorides in the pond. A simplified model showing the reaction pathway (shown in Figure 6-3) has been developed assuming the chemistry of relatively pure phosphate rock. Today's lower quality feed rock permits only a qualitative modeling of the chemical redistribution between product and waste stream.

Unless properly recognized and researched, there is the inherent risk that environmental assessments, particularly remedial actions for fluoride containment, will be fatally flawed by false chemical assumptions (9).

A thorough study of gypsum pond chemistry, namely fluorine distribution, is recommended since this can lead the way to reduced fluoride emission. The major objective of the study should be an understanding of the factors fixating fluoride in the pond or even preferably in the cake. If the redistribution of fluoride in the acidulation stage could be understood, most fluorides could be fixated in the cake where it would be ultimately disposed.

Table 9-2 shows the controlling variables of the WPPA process (9). Precipitation of fluoride dissolved from the rock is governed primarily by the interacting concentration levels of Al, Si, Na, Mg, Ca, and F released into solution from the feed rock. The quantities of these controlling constituents vary considerably and the chemistry of rock is getting more complex as the quality of rock is decreasing. In the past, with good quality rock the predominant fluoride salt was Na_2SiF_6. Rock presently used contains other fluoride salts which are frequently more soluble (e.g., $NaKSiF_6$). Precipitation of either ralstonite or chuckrovite in place of alkali fluosilicates greatly increases the amount of fluoride in the byproduct cake. The "recipe" for addition of materials leading to a chemical balance favorable to fixation of fluoride in cake would be an ultimate goal of a fluorine distribution chemistry study. A study of this nature with a limited scope is currently underway at TVA but an additional and complementary study is needed to make findings usable on a commercial level. It is not possible to estimate the cost and time-frame for such a study until a detailed scope of work is prepared.

A study of gypsum pond fluoride liquid-vapor equilibria is also recommended. Figure 9-3 shows competing equilibria governing the chemical state of fluorine (9). Assuming that SiO_2 is not a limiting constituent to establishing equilibrium, the overall reaction in solution can be expressed as:

TABLE 9-2. PARAMETERS OF F DISTRIBUTION IN DIGESTER STAGE (9)

Controlling dissolved components

Al^{3+}, Si^{4+}, Na^{+}, Mg^{2+}, F^{-}, (Ca) Al^{3+} Mg^{2+}

Sources

Apatite: Na Mg F
Accessories: Na Mg Al Si

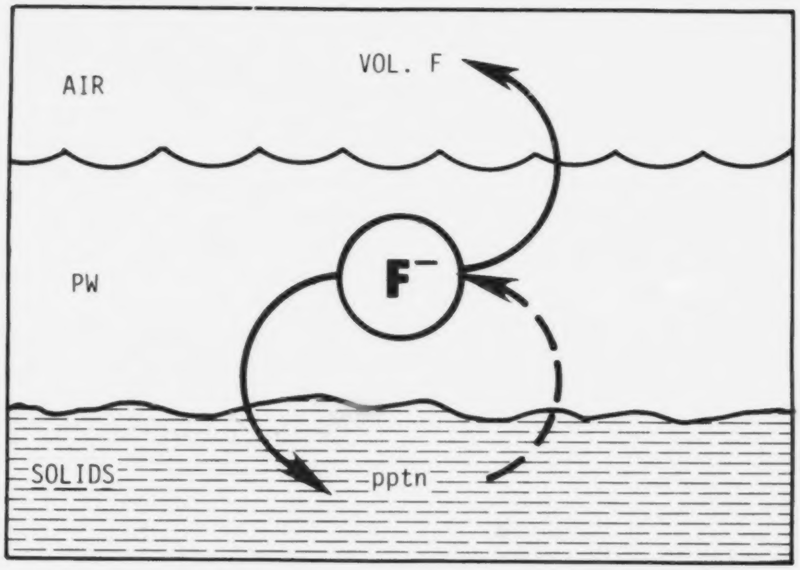
Variability (C.F.* 70 BPL)

	Mean wt. %	Obs. range
Na_2O_3	0.60	0.28-0.82
$Mg0$	0.30	0.15-0.52
Al_2O_3	1.07	0.30-1.42
$Si0_2$	4.69	2.50-7.40
F	3.78	3.60-3.90

Solubility in F.G. WPA

Apatite source: ~100%
Accessory source: Highly variable

*Central Florida


AIR
VOL. F
PW
F⁻
SOLIDS
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COMPONENTS

VAPOR PHASE: SiF_4, HF, H_2O

PW PHASE: F^-, Al^{3+}, Mg^{2+}, Si^{4+}, $(Na, K)^+$, Fe^{3+}, Ca^{2+}, PO_4^{3-}, SO_4^{2-}

SOLID PHASE: GYPSUM, F SALTS, INERTS

Figure 9-3: Competing Fluorine Chemical Equilibria (9)

$$6\ HF + SiO_2 \rightleftharpoons H_2SiF_6 + 2\ H_2O$$

and Henry's law should be applicable:

$$P_{Fv} = K \bullet C_{Fs} \text{ or } P_{Fv} = 1.58 \times 10^{-7}(C_{ppm})$$

in which

P_{Fv} = pressure (mmHg°) of total F in vapor phase

C_{Fs} = concentration (moles/liter) F in solution

C_{ppm} = concentration (ppm) F in solution

K = proportionality constant

The overall reaction sequence appears to favor HF emissions from ponds with 5,000-10,000 ppm F. Except for Reference (10) most literature examples deal with higher fluoride concentration which favors higher SiF_4 emission. It is a probable source of speculation still maintained by some industry's chemists that SiF_4 is a major emission.

The ultimate goal of pond water vapor equilibria study would be to determine the correlation between various pond composition and corresponding emissions. Such a study is well suited for an academic institution.

9.2.2 Measurement of Gypsum Pond Emissions

As mentioned in Section 6.3, actual field measurements of fluorides were carried out in 1977. The fluoride emissions from two gypsum ponds were measured by remote sensing and point sampling/analysis methods. The concentration of fluorides (primarily HF) over and at the edge of gypsum ponds was on the order of tens of ppb. Vertical traverses of fluoride concentration were obtained by a wet sampling/analysis method using a crane to position the sample. Average total fluoride emission rates for the gypsum pond were estimated to be in the range of 0.2 to 7.3 lb/acre-day.

The initial purpose of this study was to estimate the fluoride emissions rate (flux) from gypsum ponds as a function of plant operations, atmospheric conditions and gypsum pond characteristics. The data obtained during the field program were too scattered and too few to make any correlations. An additional objective of the above study was to prepare a dispersion model of fluoride emissions from gypsum ponds.

Since all of the above information is very important for further clarification of gypsum pond emissions and control, it is recommended that subsequent field measurements be carried out. The purpose of such a measurement program would be to expand fluoride emission data from the gypsum pond data base and allow correlation with atmospheric conditions and plant specifics. The upwind-downwind sampling methodology applied in TRC's study should be refined and used (11). A Gaussian dispersion model would be used in this study to simulate dispersion of fluorides emitted from the gypsum pond. The diffusion coefficients may be adjusted after the field evaluation.

A rough cost estimate of such a project is $70,000 and it could be carried out in six months.

9.3 Evaluation and Optimization of Wet Scrubbers

Wet scrubbers installed in the phosphate fertilizer industry represent the major investments for pollution control and costs run well into millions of dollars. These scrubbers control particulate, fluorides and other gaseous emissions and, as a result, most of the plants are in compliance with emission regulations. Unfortunately, most of the plants are satisfied with this fact and do relatively little to further improve scrubber efficiency and/or reduce operating cost. Although some firms collect data on scrubber performance, practically no open literature data exist that would benefit the entire phosphate fertilizer industry. There is even some doubt whether the scrubbers perform as well as claimed by the equipment vendors. Since reliable information on wet scrubber performance can result in better efficiency and lower operating and maintenance costs, two R&D programs are recommended. The first one is on scrubber optimization through a factorial design experiment; the second one includes a thorough evaluation of the IWS scrubber discussed in Section 8.3.

9.3.1 Factorial Design Experiments

The evaluation and optimization of scrubbers should be carried out on a full scale unit in a representative plant. Since the testing is relatively costly and time consuming, the testing program should be carefully planned. If the experiments are planned wisely and incorporate statistical design, correlation is often apparent and straightforward to extract (12). In order to reduce the number of runs and obtain interaction of process variables, fractional factorial design experiments are recommended. If a one-variable-at-a-time experiment is used, the interaction of important variables can be easily overlooked.

The following variables are considered important in evaluation of the efficiency of wet scrubbers:

1. Gas volumetric flow rate
2. Liquid volumetric flow rate

3. Pressure drop
4. Residence time
5. Fluoride liquid concentration

The first step in experiment planning is the screening of variables. This is a crucial step in testing where a good understanding of process variables is needed. Two or three variable levels are selected and a statistical design is carried out. Connor described the fractional factorial experiment design for factors at three levels (13). In scrubber testing two level, five variables statistical design (2^{5-2}) is recommended. Table 9-3 shows the statistical design for scrubber testing. It can be seen that eight runs are needed for the screening of variables. The following three responses are considered to be important: fluoride removal efficiency, particulate removal efficiency and energy consumption. The results of these tests could be interpreted visually for most responses. A more rigorous analysis would consist of averaging the results at the high level of the variable and subtracting the average at the low level of the variable. Thus, an estimate of the variable's main effect can be obtained.

In a full factorial design (e.g., $2^5=32$ runs) this estimate is independent of estimates of other effects. However, in a fractional factorial design the effects are confounded, which means that main effects are tied-up with interaction. As can be seen in Table 9-4, for example, the main effect of variable 1 is confounded with the interaction between variables 3 and 5. However, it is reasonably certain that some interaction in wet scrubber tests will be negligible and that most of the combined effects can be attributed to the main effect rather than an interaction.

The main objective of a screening study is to determine variables with the largest effect so that these can be optimized. If the optimum has not been approached after an initial screening study, the method of steepest ascent should be used to find the optimum region (14). Since wet scrubbers have been in operation in fertilizer plants for a number of years, it is reasonable to expect that the selection of variable values will result in near optimum conditions. An assumption is made that two variables, e.g., gas volumetric flow rate and fluoride liquid concentration, were found to have the largest effect. The optimization of these two variables will be the next step. A simple design for studying both the linear and quadratic effect of these two variables is a 3^2 equal 9 run design. Each variable is studied at three levels as shown in Table 9-5.

Based on these tests, contour surfaces for all three responses can be generated. If the optimum is really close, the contours would represent concentric ellipses with unique optimum values of the variables at the center of the ellipses (12). Again, the test results can be interpreted visually. A more rigorous statistical analysis consists of fitting the desired response with an empirical graduating function (e.g., polynomial). Such a model or regression equation would contain linear terms in the variables, an interaction term, and quadratic terms in both variables. This equation can be used as a prediction equation within the range of variables studied and would be applicable to wet scrubbers and processes similar to the one studied.

TABLE 9-3. STATISTICAL DESIGN FOR SCRUBBER TESTING

Run	X_1	X_2	X_3	X_4	X_5	Fluoride Removal Efficiency	Particulate Removal Efficiency	Energy Consumption
1	-	-	-	-	+			
2	+	-	-	+	-			
3	-	+	-	+	+			
4	+	+	-	-	-			
5	-	-	+	+	-			
6	+	-	+	-	+			
7	-	+	+	-	-			
8	+	+	+	+	+			

Variables	Hypothetical Variable Levels -	 +
1. X_1 = Gas volumetric flow rate	20,000 ACFM	25,000 ACFM
2. X_2 = Liquid volumetric flow rate	600 GPM	800 GPM
3. X_3 = Pressure drop	8 in WC	12 in WC
4. X_4 = Residence time	0.4 sec	0.6 sec
5. X_5 = Fluoride liquid concentration	5,000 ppm	8,000 ppm

TABLE 9-4. CONFOUNDING PATTERNS FOR DESIGN (2)

1	+ 3 x 5 + =	(Effect of variable 1) + (Interaction between variables 3 & 5)
2	+ 4 x 5	
3	+ 1 x 5	
4	+ 2 x 5	
5	+ 1 x 3 + 2 x 4	
1 x 2 + 3 x 4		
1 x 4 + 2 x 3		

All 3-factor interactions (e.g., 1 x 2 x 3) and higher are assumed negligible.

TABLE 9-5. OPTIMIZATION DESIGN FOR SCRUBBER TESTING

Run	X_1	X_2	Fluoride Removal Efficiency	Particulate Removal Efficiency	Energy Consumption
9	-	-			
10	-	0			
11	-	+			
12	0	-			
13	0	0			
14	0	+			
15	+	-			
16	+	0			
17	+	+			

	Variables	Hypothetical Variable Levels		
1.	X_1 = gas volumetric flow rate			+
2.	X_2 = fluoride liquid concentration	20,000 CFM	23,000 ACFM	25,000 ACFM

Cross-flow packed scrubbers are considered to be the most universal wet scrubbers for the phosphate fertilizer industry and the factorial design experiments should be carried out on one of them.

It appears that six months would be sufficient to perform such experiments. The cost for such a program is estimated to be about $100,000.

9.3.2 Performance Evaluation of Ionizing Wet Scrubbers

In the light of increased emphasis on air pollution health effects, this type of wet scrubbing equipment will be reviewed from the point of view of the respirability of effluent particles (15). Regarding particulate emissions, the main concern from the industrial hygiene standpoint is the amount of particulate deposited in the alveoli and terminal bronchioles of the respiratory system. The deposition of particulate in the pulmonary space is the function of particle size. The larger particles (above 2 microns) are readily removed in the upper respiratory system while the smaller particles (under 0.2 microns) are inhaled and exhaled. Consequently, a particle size of about 1 micron presents the main health hazard, as such particles have the maximum deposition in the alveoli (16, 17).

Section 5 of this report discussed the theory and practice of wet scrubbers with a special emphasis on particulate and gaseous removal efficiency. The particulate removal efficiency is based on two basic mechanisms: inertial impaction and diffusion. The larger particles are removed through inertial impaction while smaller ones are removed through diffusion. Because of these basic removal mechanisms, the efficiency is a function of the particle size and scrubbers operating under standard conditions have the lowest efficiency on particulate in the range of 0.1 to 1 micron. The efficiency is, therefore, the lowest on the particle size that is the most hazardous to human health.

It is important to note that dry gas cleaning devices like cyclones and filter bags have the same limitation since particulate removal in these devices is based on the same unit mechanisms. Electrostatic precipitators have also been reported to have minimum efficiency in this particle size range (18). Most of the wet scrubbers on the market today claim an efficiency of 99% and over. Unfortunately, in many cases, the basis on which the high collection efficiency claims are made is not fully described. Since the particulate emission regulations are as a rule based on a weight basis, most removal efficiencies are also reported on a weight basis. However, some scrubbers which may have a 99% efficiency on a weight basis can have a very low efficiency on a particle size basis. The best way to improve the efficiency of wet scrubbers on small particles (0.2 to 2 micron range) is to apply some basic mechanisms which are not particle size dependent. One such principle is the electrostatic charging of particulate or collecting bodies. There are a number of wet scrubbers where this principle has been applied and the ionizing wet scrubber (IWS) has been described in Section 8.4.

The evaluation of IWS scrubber efficiency in particulate removal as a function of particle size is highly recommended. It appears that this scrubber demonstrates high particulate removal efficiency regardless of particle size distribution. The verification of this fact is very important for the reduction of the above described health hazards and its application, as well as the application of similar devices, could go well beyond the phosphate fertilizer industry.

The major purpose of this evaluation will be to measure the particulate removal efficiency as a function of the particle size distribution and determine optimum operating conditions. The test should be carried out through simultaneous sampling of the IWS scrubber inlet and outlet and subsequent measurement of the particle size distribution. The important range of particle size distribution is in the range of 0.02 to about 5 microns. The determination of particle size range is not straightforward and the reliability of this experiment will probably be limited by such measurements. A recently developed cascade impactor system for sampling 0.02 to 20 micron diameter particles can be applied to this study (19). The new sampling train components were designed to accompany the UW Mark 3-4 Source Test Cascade Impactor. This train was designed to sample in-situ at both the inlet (high concentration) and the outlet (low concentration) of particulate control devices applied to coal-fired utility boilers. Figure 9-4 shows the actual particle size distribution for tests at a Generating Station (19). This instrument can be applied for measurement of particulate size distribution in a phosphate fertilizer plant. Since there is a growing concern that fluoride emissions from DAP plants are submicron particles, the IWS tests should be performed on DAP plant emissions. The operating parameters should be varied in the course of testing in order to obtain optimum conditions for particulate removal. Possibly fractional factorial design experiments described in a previous section could be used for this evaluation.

These tests could be performed within six months; the cost is unknown as it will probably depend on the complexity of particle size distribution measurements.

9.4 Ammonia-Sulfuric Acid Mist Interaction Atmospheric Chemistry and Dispersion Modeling Study

Frequently, manufacturing activities for inorganic acids (sulfuric and nitric acid) and inorganic fertilizers are concentrated within one industrial area (frequently even within one plant). Because of the proximity of points of emissions, the interaction between the various air pollutants can have synergistic effects on the environment and on air quality. Of particular interest and potential for interaction are sulfuric acid mist emitted from sulfuric acid manufacturing plants, and ammonia emitted from DAP plants and nitrate fertilizer facilities. Possible uncontrolled emissions from each manufacturing activity are given in Table 9-6. Interaction between ammonia and sulfuric acid mist will result in formation of ammonium sulfate particles which will lead, at high relative humidity, to particle growth due to condensation and thus to visibility impairment.

Since ammonium sulfate, ammonium nitrate and sulfuric acid have different deliquescence points (62% RH for NH_4NO_3 80% RH for $(NH_4)_2SO_4$ and ≈70% RH for

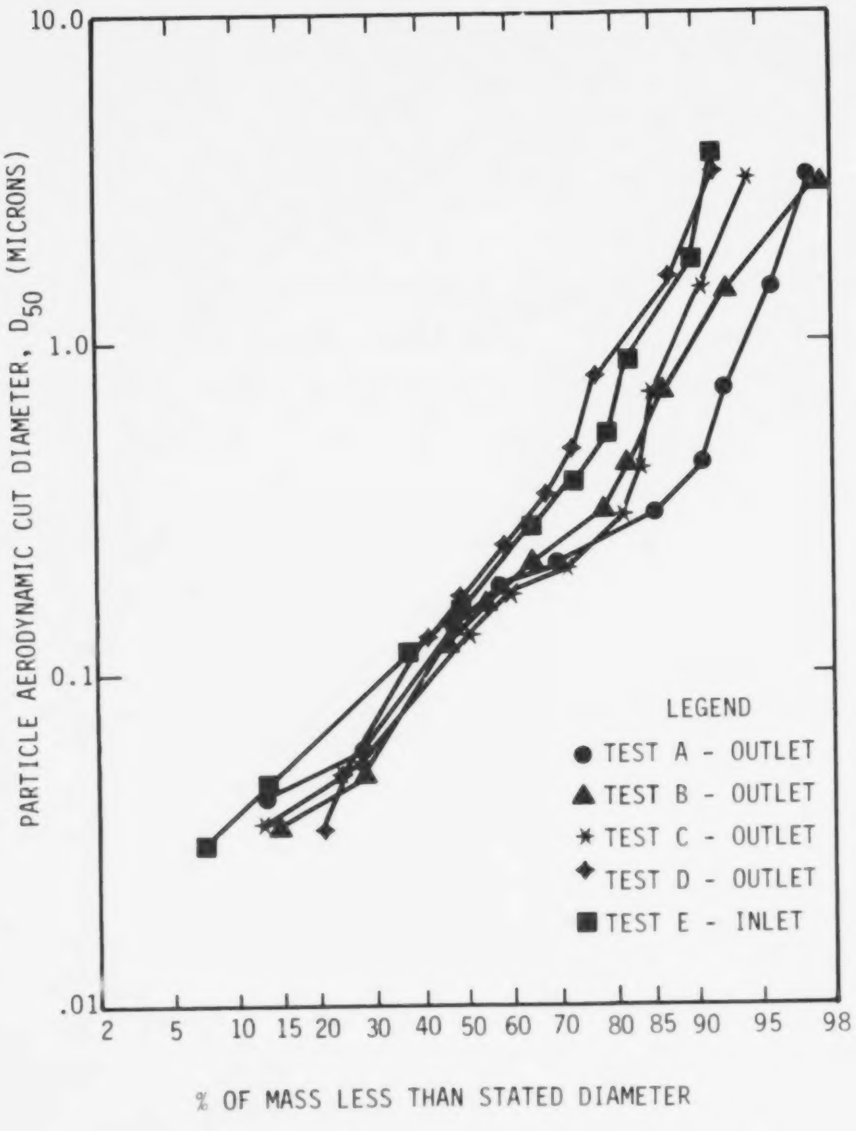

Figure 9-4: Particle Size Distributions Tests A-E, Kearny Generating Station (19)

TABLE 9-6. EMISSION FACTORS OF SOME INDUSTRIAL ACTIVITIES (20)

Manufacturing Activity	Pollutant Emitted	Emission Factor kg/MT
H_2SO_4	Acid Mist	3.75
Ammonia	Ammonia	100.
Ammonium Phosphate	Ammonia	
Ammonium Nitrate	Nitric Oxides (as NO_3)	2
	Ammonia	2.5 - 3.
Urea	Ammonia	25 - 50
Triple Phosphate	Ammonium Chlorine	

H_2SO_4), the transformation from one species to the other can have a marked effect on the particle size distribution within the plume. Since the scattering coedfficient (b_{scat}) is a function of the square of the particle diameter, a change in particle size distribution will cause a significant effect on visibility.

In order to fully understand the potential effect of the interaction of ammonia and sulfuric acid mist on visibility, the following studies are necessary:

1. Development of a model that will describe the interaction of two plumes and will incorporate an aerosol dynamics model. The required model will describe the dispersion of two plumes as independent entities until "point" of interaction. After interaction the model should incorporate the chemical reaction between ammonia and sulfuric acid (the reaction will, probably, be diffusion control.) At this stage, the model should also include an aerosol dynamics model that will calculate the evolution with time of the aerosol size distribution as a function of aerosol composition and relative humidity.

2. Experimental studies on the interaction between gaseous ammonia and sulfuric acid mist and its effect on the optical properties of the atmosphere, at different relative humidities. Experimental studies should be conducted in a chamber with controlled relative humidity into which acid mist aerosol could be injected (via a vibrating needle aerosol generator, for example) together with gaseous ammonia. The change, in time, of transmitted light attenuation and/or light scattering should be measured. This study can be accomplished within 6 months at an approximate cost of $100,000.

9.5 Demonstration of Dry Fluoride Removal System

One of the major roles of the gypsum pond system is to cool and recycle scrubbing liquid used for emission control. Recycled scrubbing liquid is used for the reduction of the gas temperature needed to reach the low levels of fluoride emissions. It is estimated that approximately half the thermal load in the fertilizer complex results from the emission control (21). The dry chromatographic technique can accomplish the same function as wet scrubbers, namely simmultaneous emission of particulate and gaseous emissions. In this technique no cooling is necessary so that a pond is not needed.

The dry chromatographic system has been used in the secondary aluminum and glass industries. Figure 9-5 shows the system as used on secondary aluminum smelters (22). This dry chromatographic system consists of an evaporation chamber, baghouse and blower. The blower induces discharge gases for the stack hoods into the inlet duct work. The gases are respectively cooled by water punching and air blending to a range of 160°F to 220°F before entering the baghouse. The filter bags are protected from blinding and burning by application of a chromatographic coating. The coating absorbs and neutralizes acid gases. It is applied batch wise to the bags through precoated inlet ducts. Once applied, the coating is effective for

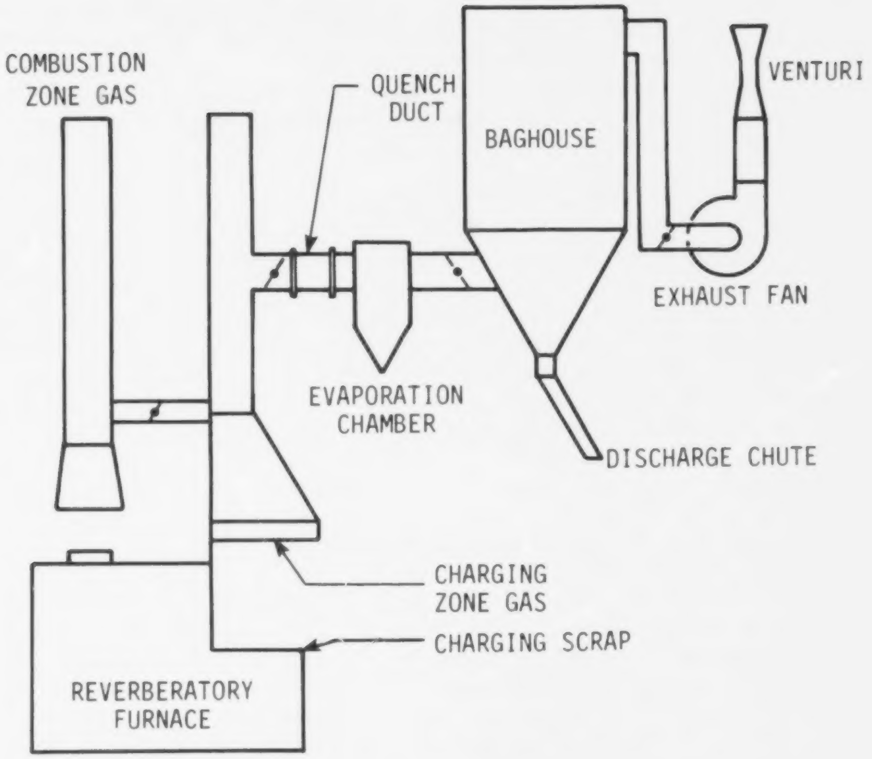
COMBUSTION ZONE GAS
QUENCH DUCT
BAGHOUSE
VENTURI
EXHAUST FAN
EVAPORATION CHAMBER
DISCHARGE CHUTE
CHARGING ZONE GAS
CHARGING SCRAP
REVERBERATORY FURNACE

Figure 9-5: Dry Chromatographic System (22)

several days, during which time the system may be left unattended. Table 9-7 shows the performance of a TESI dry chromatographic system on three applications.

The application of this system to phosphate fertilizer emissions is expected to reduce pond size 50 to 67%. Total fluoride pond emissions are expected to be reduced as much as 85%. Inasmuch as no cooling is required for this application, a load of 150,000,000 BTU/hr normally imposed on the ponds is circumvented. The gaseous fluorides are removed at elevated temperatures using a dry collector as the reactor. Submicron particulates (i.e., $NH_4F \bullet HF$) are also agglomerated by the chromatographic technique. Gaseous fluoride emissions are expected to be reduced to 1 ppm and particulate to less than 0.01 gr/sdcf.

Table 9-8 shows the performance of existing wet scrubbing TESI equipment at two plants and the projections for the dry chromatographic system (21). The cost of dry chromatograph material (TESISORB) is \$0.07/ton P_2O_5. The consumption of TESISORB is estimated to be less than \$50/day and the quantity of neutralized product about a ton per day. The neutralized product can be mixed with the fertilizer product and discharged from the plant. The power consumption should be reduced 20% because of reduction in liquid pumping.

Figure 9-6 shows the flow sheet for a proposed demonstration pilot dry fluoride removal system. It is recommended for use on emissions from a diammonium phosphate plant. This way its effectiveness in the removal of fluoride and submicron particulate can be demonstrated.

The gases from the process will be first introduced into a quench reactor where they will be treated with a mixture of water and calcium hydroxide. Some fluorides will be absorbed by the alkaline solution and gas will be cooled on its way to the chromatographic separator. Gas will then be passed through a dry Venturi. A dry Venturi exhibits high efficiency in removal of submicron particulate. TESISORB particles are injected into a gas stream where they serve as the collection bodies for the collection of particulate.

Although most of the particulate is in the submicron range, high efficiency is achieved at a very low pressure drop. The reasons for this have been previously presented in Section 5.1. The efficiency of particulate removal in the Venturi throat is governed by the inertial impaction parameter. Since the diameter of collection bodies (TESISORB particulate) is very small, a high efficiency can be achieved. The final removal of TESISORB and particulate is accomplished in a chromatographic separator. The solids from the chromatographic separator will be removed from the separator. The solids can then be washed on a rotary filter, dried and returned to the dry Venturi.

The major purpose of this demonstration project will be to verify applicability of dry fluoride removal in the phosphate fertilizer industry. Experimental and measurement techniques described in previous recommended projects can be also applied in this demonstration. The design parameters for a full scale system will be obtained in this project. The cost for the installation will be in the range of \$100,000 to \$200,000 depending on the complexity of the auxiliary equipment. The unit can be built in six months and testing carried out during the subsequent six months.

TABLE 9-7. PERFORMANCE OF CHROMATOGRAPHIC SYSTEMS (23)

	PARTICULATE		ACID GAS	Opacity
	gr/dscf	g/dncm	ppm	Percent
Secondary Aluminum				
Inlet, 0.03-0.35 gr/dscf	0.00056	0.0013	0.5	Zero
0.69-80 g/dncm	to 0.008	0.0183		
30 percent Oils				
Hcl, 10-150 ppm				
Cl_2, 0-100 ppm				
HF, 0-30 ppm				
Container Glass				
Inlet, 0.15-0.3 gr/dscf	0.005-0.01	0.011-0.023	$SO_3 < 1$	Zero
0.34-0.69 g/dncm			SO_2 10-60	
SO_3, 20-40 ppm				
SO_2, 100-180 ppm				
Fiberglass				
Inlet, 0.15-1.3 gr/dscf	0.001-0.008	0.002-0.018	HF< 2	Zero
0.34-2.98 g/dncm			SO_x <40	
HF, 100-150 ppm				
SO_x, 200-300 ppm				

TABLE 9-8. PERFORMANCE OF TESI EQUIPMENT

	EPA	Plant 1 1967 (550 TPD)	Plant 2* 1973 (1100 TPD)	Third*** Generation TESI
Acidulation lb/ton P_2O_5	0.02	0.003		0.002
DAP lb/ton P_2O_5	0.06	0.04	0.02	0.010
GTSP lb/ton P_2O_5	0.2		0.04	0.020
GTSP Storage lb/ton P_2O_5 in storage	5×10^{-4}		2×10^{-4}	1×10^{-4}
Pond Fluoride emission lb/day		30	30	15 (Gyp Only)
Total lb/day F (stacks)		27	45-60**	

*No ammonia to pond
**Plant reports 35-50% of guaranteed emissions.
***Dry chromotographic technique.

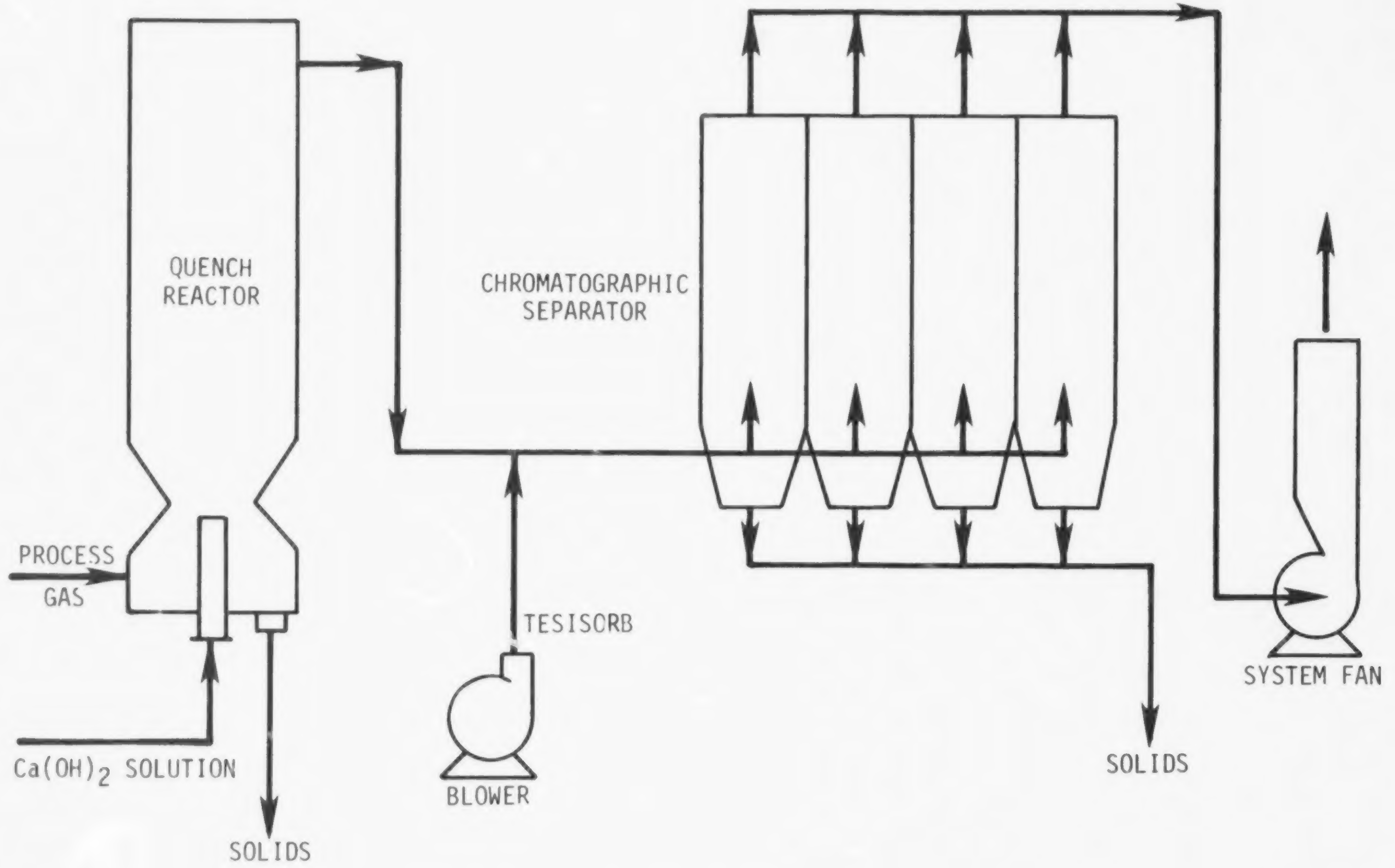
QUENCH REACTOR
PROCESS GAS
$Ca(OH)_2$ SOLUTION
SOLIDS
CHROMATOGRAPHIC SEPARATOR
TESISORB
BLOWER
SOLIDS
SYSTEM FAN

Figure 9-6: Pilot Dry Fluoride Removal System (25)

9.6 Evaluation of the Kimre Mist Eliminator

In the past, one of the major problems with wet scrubbers in the phosphate fertilizer industry has been maintenance. Packing and mist eliminators have a tendency to plug and cleaning is a tedious and time consuming process. During recent years many wet scrubbers have been retrofitted with Kimre mist eliminators. These mist eliminators are made of various materials and utilize interlaced monofilaments with essentially all of the filaments oriented perpendicular to the gas flow. They are very stable, both dynamically and statically, since each filament reinforces those closest to it. This makes these eliminators very easy to clean, and is a major reason for their popularity.

The amount of liquid passing through the eliminator without being captured may be expressed as:

$$Pt = \exp.(-K_1 N)$$

Where Pt = penetration (1-efficiency); fractional amount passing

N = number of layers

K_1 = variable relating the geometry of the material, droplet size, and gas velocity with drop removal effectiveness

K_1 must be determined experimentally. For one Kimre mist eliminator, the value of K_1 for the removal of 3 micron droplets at a gas velocity of 5 feet per second has been determined to be 0.452 (24). Using this value, N may be determined from:

$$N = -\frac{\ln(Pt)}{K}$$

For an efficiency of 99.9%,

$$N = -\frac{\ln(1 - 0.999)}{0.452} = 15.28,$$

so that 16 layers must be used.

The pressure drop through a mist eliminator may be expressed as:

$$\Delta p = K_2 \bullet V^2 \bullet N,$$

where Δp = pressure drop, includes H_2O

K_2 = variable relating material geometry, liquid loading and pressure drop

V = gas velocity, feet per second

N = number of layers.

K_2 for low liquid rates and air at standard atmospheric conditions is 1.71×10^{-3}.

The pressure drop for the eliminator in the example cited above is:

$$\Delta p = 1.71 \bullet 10^{-3} \bullet 5^2 \bullet 16 = 0.68 \text{ in. } H_2O$$

Although Kimre mist eliminators have been widely used in the phosphate fertilizer industry, there is little information on their performance. According to the manufacturers these mist eliminators have performed substantially better than theory would predict for the small droplets.

An evaluation of the Kimre mist eliminator is recommended in order to establish its performance and obtain optimum operating conditions. The evaluation can be carried out on a prototype scrubber/mist eliminator shown in Figure 9-7. The advantage of this unit is that it consists of multiple layers of different size with the larger being in front to prevent plugging and insure easy cleaning. The main purpose of the evaluation would be to obtain reliable performance data applicable to the phosphate fertilizer industry.

The cost of the unit is unknown, but testing can be accomplished at a cost of $30,000 within four months.

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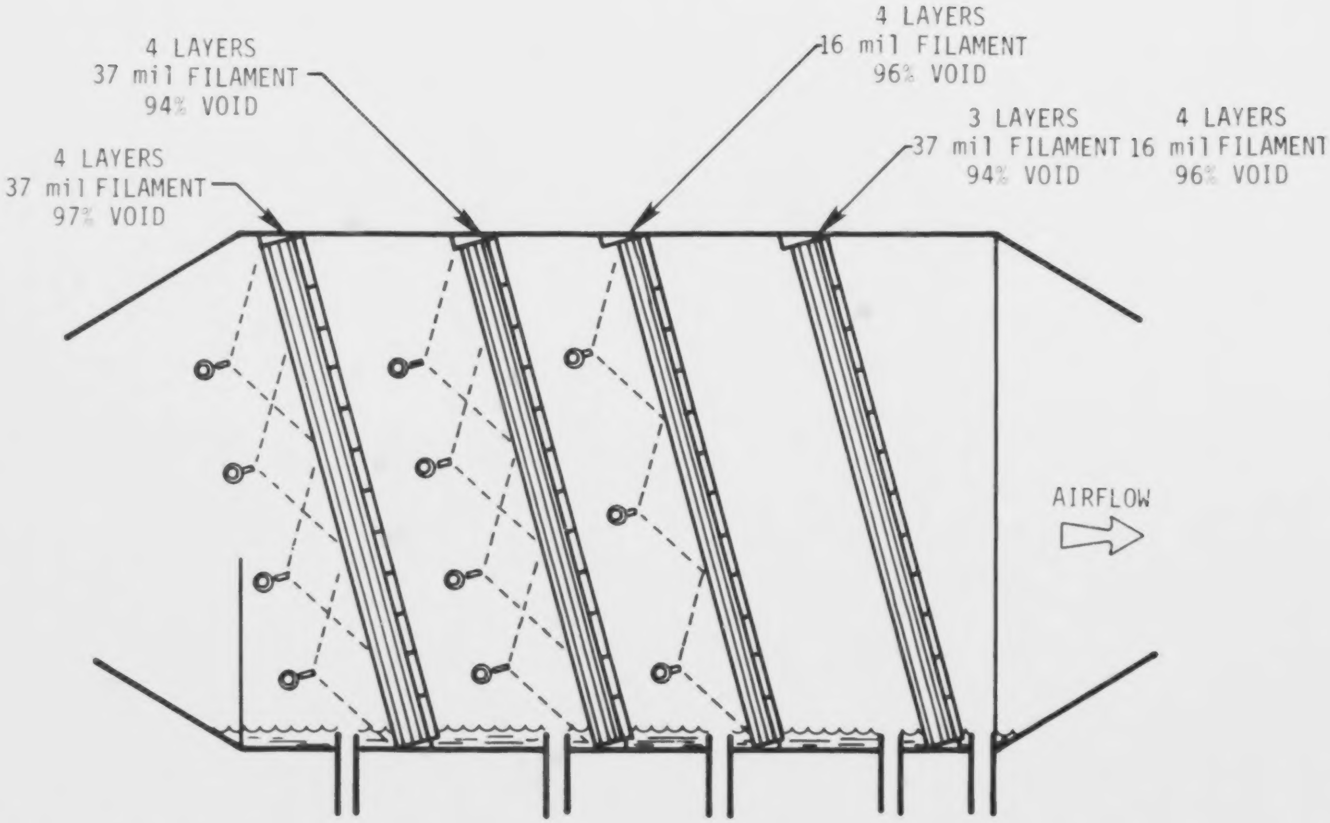
4 LAYERS
37 mil FILAMENT
94% VOID
4 LAYERS
16 mil FILAMENT
96% VOID
4 LAYERS
37 mil FILAMENT
97% VOID
3 LAYERS
37 mil FILAMENT
94% VOID
4 LAYERS
16 mil FILAMENT
96% VOID
AIRFLOW

Figure 9-7: Four Stage Scrubber/Mist Eliminator (26)

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1) Process Description
2) Air Emissions and Controls
3) Wastewater Sources and Treatment
4) Solid Waste
5) Miscellaneous

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